UNIVERSAL
LIBRARY

117 565

UNIVERSAL
LIBRARY

q665.5 D92s v.5,pt.1

[redacted]

THE SCHOOL DISTRICT OF KANSAS CITY, MISSOURI

This Volume is for
REFERENCE USE ONLY

THE SCIENCE OF PETROLEUM

VOLUME V PART I

CRUDE OILS

CHEMICAL AND PHYSICAL PROPERTIES

THE SCIENCE OF PETROLEUM

A COMPREHENSIVE TREATISE OF THE PRINCIPLES AND PRACTICE OF THE PRODUCTION, REFINING, TRANSPORT, AND DISTRIBUTION OF MINERAL OIL

VOLUMES I, II, III, IV

Edited by

DR. A. E. DUNSTAN

PROFESSOR A. W. NASH

DR. BENJAMIN T. BROOKS

SIR HENRY TIZARD, K.C.B., F.R.S.

VOLUME V

Edited by

DR. BENJAMIN T. BROOKS

DR. A. E. DUNSTAN

THE SCIENCE OF PETROLEUM

VOLUME V PART I

CRUDE OILS

CHEMICAL AND PHYSICAL PROPERTIES

General Editors
DR. BENJAMIN T. BROOKS
DR. A. E. DUNSTAN

OXFORD UNIVERSITY PRESS
LONDON NEW YORK TORONTO
1950

ADVISORY EDITORS
DR. M. R. FENSKE
PROF. F. H. GARNER
DR. E. R. GILLILAND
DR. J. BENNETT HILL
DR. D. A. HOWES
DR. E. V. MURPHREE
DR. FREDERICK D. ROSSINI
DR. K. M. WATSON

PRINTED IN GREAT BRITAIN

FOREWORD

PETROLEUM technology has advanced tremendously during the past several years. In the field of production knowledge of the factors that lead to more efficient recovery of oil from the earth has been greatly extended. This is reflected in a large increase in recoverable oil reserves. In the refining field many outstanding new processes have been developed, such as catalytic cracking, alkylation, production of synthetic toluene, and production of synthetic rubber and its raw materials from petroleum. As a result of these and other developments, refining has become, to a considerable extent, a large-scale, organic synthesis operation wherein selected classes of materials are produced. The advances in petroleum technology have been too rapid for the literature in the field to give a reasonably complete picture of developments, and text-books are not available which fully reflect the changes.

The editors and the publisher of the new volumes of the *Science of Petroleum* are, therefore, to be congratulated on the real contribution they have made in providing in usable form an authoritative reference which brings up to date our information on petroleum technology. It is particularly fortunate that these volumes will appear at a time when there is such definite need for sound information on the nature and influences of the new techniques that to-day characterize the petroleum industry. The leading petroleum technologists who have contributed papers are to be highly complimented. Their efforts reflect the progressive spirit of the petroleum industry in co-operating to render a service to the public.

NEW YORK
1949

R. T. HASLAM

PREFACE

SO many and so far-reaching have been the technological advances made since 1937, when the first four volumes of the *Science of Petroleum* were compiled, that supplementary volumes have become necessary.

Volume V, of which this book is the first Part, deals with the Chemistry, Physics, and Chemical Engineering of Petroleum. It is hoped to issue in due course two further parts which will complete the work of bringing up to date this section of the subject.

Volume VI will deal with the Geology, Geophysics, Production, and Distribution of Petroleum and will be edited by Professor V. C. Illing, F.R.S., of London, and F. R. Suman, B.S., D.Eng., of New York.

Petroleum technology is international. The oilfields of the world are widely distributed, but the fundamental principles of production, refining, and distribution are the concern of all who have a part to play in this great industry.

In the recent war years greater progress has been made in the United States than in Europe where research was of necessity restricted. Of outstanding importance, therefore, are the contributions from Americans, and these form the greater part of this volume.

Most of the material in the first four volumes of the *Science of Petroleum* is of permanent value, and these volumes are still available. The contributions in the present volume fall into two classes, those which deal with subjects and processes which are new in the industry since 1937, and those which supplement and bring up to date subjects which were thoroughly covered in the earlier volumes.

The technical and scientific literature concerned with petroleum, as in the case of other great industries, is scattered through a large number of excellent technical journals. Their number is beyond the capacity of any except the large and relatively complete libraries. It has been our purpose, therefore, to bring together this record for the past twelve years by means of contributions by authors of the highest standing who are able to review and evaluate this mass of literature, thus giving to the petroleum world a continuous exegesis of the development of its science and technology. Such a task is increasingly difficult and costly, and the present undertaking has been made possible only by the generous co-operation of the contributors and the broad policy of the publishers in supporting, without subsidy from the industry, this undertaking. The continuation of this work depends to a great degree on the interest taken in this volume by all concerned, whether executives or scientific personnel.

We record with regret the death of one of the original four editors, Professor A. W. Nash, during the war, and the withdrawal of another, Sir Henry Tizard, owing to pressure of other duties. As already mentioned, Professor Illing and Mr. Suman fill their places. It is also with great regret we announce the death of Dr. Whitmore whilst his article was in the press. Dr. Whitmore probably did more to advance the chemistry of the aliphatic hydrocarbons than anyone in recent years.

We would like to express our gratitude for the great help we have received from those whose names are given as our advisory editors, and from the contributors.

B. T. B.
A. E. D.

CONTENTS

VOLUME V

PART I

Section I. CRUDE OILS 1

The Crude Oils of the U.S.A., 1935–45 . . H. M. SMITH . . . 3
The Crude Oils of Venezuela . . . GULF REFINING COMPANY . 21
The Crude Oils of Saudi Arabia . . . ARABIAN–AMERICAN OIL COMPANY 22
The Crude Oils of Bahrein Island . . . J. R. KEITH . . . 28
The Crude Oils of the Middle East . . . D. A. HOWES and L. C. STRANG . 30
Evaluation of Crude Oils and Oil Stocks . . W. L. NELSON . . . 35
Economic Developments in the Petroleum Industry . O. TOKAYER . . . 42

Section 2. CHEMICAL AND PHYSICAL PROPERTIES OF PETROLEUM HYDROCARBONS 53

Hydrocarbons in Petroleum . . . . A. N. SACHANEN . . 55
The Chemistry of Paraffin Hydrocarbons . . J. HABESHAW . . . 78
The Chemistry of Naphthene Hydrocarbons . W. J. OLDHAM . . . 85
The Chemistry of Aromatic Hydrocarbons . . W. J. OLDHAM . . . 89
The Chemistry of Olefine and Diolefine Hydrocarbons . . . . F. A. FIDLER . . . 98
Mechanism of Organic Reactions . . . F. C. WHITMORE and N. C. COOK 114
The Fractionation, Analysis, and Isolation of Hydrocarbons in Petroleum . . . . B. J. MAIR and F. D. ROSSINI . 126
Chemical Thermodynamic Properties of Hydrocarbons . . . . F. D. ROSSINI . . . 153
High-Pressure Vapour–Liquid Equilibria in Cycling Operations . . . . . . D. L. KATZ and M. J. RZASA . 182

INDEX 193

SECTION 1

CRUDE OILS

The Crude Oils of the U.S.A. 1935–45 . H. M. SMITH
The Crude Oils of Venezuela . . GULF REFINING COMPANY
The Crude Oils of Saudi Arabia . . ARABIAN–AMERICAN OIL COMPANY
The Crude Oils of Bahrein Island . . J. R. KEITH
The Crude Oils of the Middle East . D. A. HOWES and L. C. STRANG
Evaluation of Crude Oils and Oil Stocks . W. L. NELSON
Economic Developments in the Petroleum Industry . . . . O. TOKAYER

THE CRUDE OILS OF THE U.S.A., 1935–45

By HAROLD M. SMITH

Principal Petroleum Chemist, Bureau of Mines, U.S. Dept. of the Interior

Introduction

THE crude oils of the United States are of the utmost importance in to-day's national economy, which relies so greatly on the application of machines—machines that derive their motivating energy, in increasing extent, from petroleum products. During the last two decades great improvements have been made in the methods for converting the potential energy of liquid fuels into mechanical motion, and these improvements have necessitated changes of major importance in the fuels and lubricants for the engines. In order to make these changes, increased knowledge regarding the composition and properties of the fuels and lubricants has become necessary, and the older methods of analysing and evaluating crude oils are becoming obsolete.

In this article the analyses of several hundred crude oils are summarized, and these analyses were made by a method that has been used by the Bureau of Mines for 25 years. Admittedly such analyses cannot meet the demands for detailed information that are required to-day, and for that reason have been supplemented when possible by more detailed data regarding the composition and properties of crude oil fractions. The older-type analysis still serves a useful purpose in presenting a 'snapshot' of the crude oil that permits quick judgement of its possibilities as a source of specific hydrocarbons, fuels, and lubricants. Also, as more detailed data accumulate correlations between them and the standardized routine analyses become possible. Finally, there are at present no analyses on all types of crude oil from all over the world on a comparable basis, except those of the Bureau of Mines.

Volume II of this treatise contains three articles describing the characteristics of United States crude oils from California [27, 1938], the Mid-Continent area [40, 1938], and the Gulf Coast area [18, 1938]. The data for oils from California and the Gulf Coast cover the producing fields in those areas adequately up to 1935 and include many fields important to-day, but the data on Mid-Continent oils were not as extensive, and do not include many fields now important from the production viewpoint. In preparing the present article an attempt has been made to cover all important producing fields in the United States as of 1 January 1946, including production figures, but avoiding duplication of other data previously reported.

In an article such as this it would not be practicable to include analyses for crude oils from each of the many thousands of oilfields and producing horizons in the United States. Accordingly, selection has been made on the basis of total production in 1945 and on estimated reserves.[1] The fields thus selected represent 76·4% of the total United States production in 1945 and 82·0% of the estimated reserves as of that date.

In many fields there are two or more producing horizons, from which oils of different characteristics may be produced. In the analytical data given the oil from the most prolific production zone has, if possible, been selected. Most of the analytical data are compiled from analyses made at the Bureau of Mines Petroleum Experiment Station, Bartlesville, Oklahoma, and a few at the Bureau Petroleum and Oil Shale Experiment Station, Laramie, Wyoming.

Tabulated Data

As the essence of this article is in its tabulated data, a clear description of the contents of each table is essential.

Table I. Table I presents production data for United States crude oils as of 1 January 1946 for all fields which either produced 1,000,000 barrels or more of oil in 1945 or have an estimated recoverable reserve of 10,000,000 bbl. or more, plus a few additional fields of interest because of potential future development. It also (columns 1, 2, and 7) serves as an index to the analytical data.

Column 1 lists item numbers, which are used in the subsequent tables where analytical data on crude oils from these fields are presented.

Column 2 lists the fields alphabetically by State and field names (for California, Louisiana, and Texas, by districts, with the fields given alphabetically for each district).

The discovery year of each field is given in column 3, taken from the *Transactions of the American Institute of Mining and Metallurgical Engineers* [1, 1945].

The annual production for 1945 and the cumulative production through 1945 are given in columns 4 and 5. These data, in thousands of barrels, were taken from the *Oil and Gas Journal* [29, 1946].

Column 6 presents estimated reserves, also taken from the *Oil and Gas Journal* [29, 1946].

Column 7 is a cross-reference index to other tables, both in this article and in Volume II of this treatise, where analytical data are given for crude oils from the fields listed. The roman numerals refer to tables in the present article, the arabic numerals in parentheses '(1)' are bibliography references to articles in Volume II of this work.

Table II. Table II presents summarized data obtained by application of the Bureau of Mines method of routine analysis of crude oils. This method has been described briefly by Kraemer [18, 1938; 19, 1937] and in detail in Bulletin 207 [11, 1922]. Interpretations of results are discussed in Report of Investigation 3279 [23, 1935] and Bulletin 291 [31, 1928]. The table has been divided into the following sections:

A. Arkansas
B. California
C. Illinois
D. Kansas
E. Louisiana
F. New Mexico
G. Oklahoma
H. Texas
I. Wyoming
J. Colorado, Florida, Indiana, Michigan, Mississippi, Montana, Nebraska, and Pennsylvania.

The fields are listed alphabetically under each section or under State subdivisions.

Column 1 gives the item number that refers directly to the same item number of Table I. It will be noted that all item numbers are not represented, either because the pertinent data are given in Vol. II [18, 27, 40, 1938] or because no analyses were available.

---

[1] Estimated reserves include only those oils that can be reasonably expected to be ultimately recovered by known production methods.

TABLE I

Production Data for United States Crude Oil

Item No. (1)	STATE *Field* (2)	*Discovery Year** (3)	*Annual production†*		*Estimated reserves†* (6)	*Analytical Tables‡* (7)
			1945 (4)	*Cumulative* (5)		
	ARKANSAS					
1	Atlanta	1938	1,337	6,353	9,913	II–A
2	Magnolia	1938	4,963	41,152	59,187	II–A
3	McKamie	1940	1,115	4,293	13,195	II–A
4	Midway	1942	2,642	8,401	31,704	II–A
5	Schuler and East	1937	4,693	47,843	36,847	II–A
6	Smackover	1922	4,130	407,051	43,060	(40), IV
7	Stephens	1941	2,014	12,795	15,205	II–A
	Total	..	20,894	..	..	..
	% of U.S. total	..	1·22	..	..	..
	CALIFORNIA					
	San Joaquin Valley Fields					
8	Antelope Hills	1942–4	681	2,208	7,778	II–B
9	Belridge, No.	1912	2,328	51,800	18,199	III (27)
10	Belridge, So.	1911	4,651	35,173	36,818	III (27)
11	Buena Vista Hills	1909	15,759	315,373	104,626	(27)
12	Canal	1937	1,252	11,649	18,349	II–B
13	Coalinga, East	1900	7,563	249,824	75,184	(27)
14	Coalinga-Guijarral Hills	1938	21,096	98,255	281,743	II–B, III, VI, VII, VIII
15	Coalinga West	1900	2,890	156,235	28,766	(27)
16	Coles Levee, No.	1938	6,008	25,550	74,453	II–B, VI
17	Edison	1934	2,141	13,643	25,360	(27)
18	Elk Hills	1919	15,813	191,064	243,936	III, VI (27)
19	Fruitvale	1928	3,097	35,746	24,242	(27)
20	Greeley	1936	5,062	24,145	40,854	II–B, III
21	Kern Front	1925	4,686	64,473	42,104	(27)
22	Kern River	1900	3,547	294,282	35,721	(27)
23	Kettleman North Dome	1928	14,349	310,052	130,454	III (27)
24	Lost Hills	1910	1,218	57,760	12,239	(27)
25	McKittrick-Cymric	1898	2,017	99,963	21,742	(27)
26	Midway–Sunset	1900	14,373	690,338	129,651	III (27)
27	Mountain View	1933	1,021	45,140	11,662	III (27)
28	Mount Poso	1927	6,726	86,108	69,940	(27)
29	Paloma	1939	812	2,819	25,461	II–B
30	Pleasant Valley	1943	1,309	2,479	15,020	II–B
31	Rio Bravo	1937	5,732	33,462	66,538	II–B, III
32	Riverdale	1941	1,577	3,779	14,463	II–B, III
33	Round Mountain	1927	3,506	46,703	33,540	(27)
34	Ten Section	1936	4,105	35,682	54,311	II–B, III
	Coastal Fields					
35	Aliso Canyon	1938	1,152	5,431	19,969	II–B
36	Capitan	1929	767	9,516	14,984	III (27)
37	Del Valle	1940–1	1,916	5,607	20,442	II–B
38	Elwood	1927	2,171	75,163	21,837	(27)
39	Gato Ridge	1931	1,607	11,401	15,596	(27)
40	Newhall-Potrero	1937	1,980	9,434	24,310	II–B
41	Padre Canyon	1936	750	3,444	10,555	II–B
42	Rincon	1927	1,660	19,490	18,259	III (27)
43	San Miguelito	1931	1,928	12,911	42,091	III (27)
44	Santa Maria	1902	5,057	158,004	73,814	(27)
45	Santa Maria Valley	1934	13,538	63,034	107,043	III (27)
46	Ventura Avenue	1926	17,663	303,113	206,884	III (27)
47	Ventura-Newhall	1876	2,255	71,740	20,992	(27)
	Los Angeles Basin Fields					
48	Brea Olinda	1897	4,194	176,858	44,135	III (27)
49	Coyote, East	1911	1,831	51,488	23,515	III, VI (27)
50	Coyote, West	1909	5,266	144,413	50,587	III, VI (27)
51	Dominguez	1923	6,722	162,007	72,992	III (27)
52	Huntington Beach	1920	17,558	361,588	168,409	III (27)
53	Inglewood	1924	5,640	151,589	48,401	III, VI (27)
54	Long Beach	1921	9,803	712,419	95,585	III (27)
55	Montebello	1917	3,658	142,940	30,265	III, VI (27)
56	Richfield	1919	2,725	106,404	25,593	(27)
57	Rosecrans	1924	2,087	57,578	19,916	III (27)
58	Santa Fe Springs	1921	6,258	502,820	64,680	III (27)
59	Seal Beach	1926	3,425	102,046	40,454	III (27)
60	Torrance	1922	3,244	117,097	35,395	III (27)
61	Wilmington	1937	36,222	281,478	350,730	II–B, III
	Total	..	314,396	..	..	..
	% of U.S. total	..	18·37	..	..	..

* Reference (1).

† Reference (29). Data in thousands of barrels.

‡ Roman numerals refer to tables in this article, Arabic numerals are reference numbers in bibliography to articles in Vol. II of this treatise.

TABLE I *(cont.)*

Item No. (1)	STATE *Field* (2)	*Discovery Year** (3)	*Annual production†*		*Estimated reserves†* (6)	*Analytical Tables‡* (7)
			1945 (4)	*Cumulative* (5)		
	COLORADO					
62	Rangely	1933–4	1,495	3,444	164,556	II–J
63	Wilson Creek	1938	1,997	5,561	28,009	II–J
	Total	..	3,492	..	..	..
	FLORIDA					
64	Sunniland	1943	27	43	..	II–J
	ILLINOIS					
65	Bridgeport	..	2,144	234,013	20,016	II–C
66	Centralia	1937	1,729	27,644	16,030	II–C
67	Clay City Cons.	1937	5,104	41,861	19,339	II–C
68	Dale-Hoodville	1940	2,022	21,244	10,108	..
69	Louden	1937	9,463	121,283	40,417	II–C, IV
70	New Harmony	1939	3,429	32,152	18,551	II–C
71	Noble	1937	2,739	19,672	14,666	II–C
72	Robinson	..	1,095	152,158	15,400	II–C
73	Salem	1938	6,637	192,194	23,548	II–C
	Total	..	34,362	..	..	..
	% of U.S. total	..	2·00	..	..	..
	INDIANA					
74	Griffin	1938	1,698	19,082	..	II–J
	% of U.S. total	..	0·10	..	..	..
	KANSAS					
75	Bemis-Shutts	1935	5,160	37,702	23,766	II–D, VI
76	Bloomer	1936	2,902	21,611	17,770	II–D
77	Burnett	1937	3,189	21,908	25,092	II–D, VI
78	Chase	1931	3,076	40,394	15,380	II–D
79	Geneseo	1934	2,235	17,079	12,403	II–D
80	Gorham	1941	2,068	29,076	15,927	II–D
81	Hall-Gurney	1931	3,410	26,080	28,876	II–D
82	Kraft-Prusa	1937	4,590	19,538	27,540	..
83	Silica	1931	5,868	66,988	40,040	II–D, VI
84	Trapp-Sellens	1939	10,631	72,887	61,947	II–D
85	Zenith	1937	2,912	20,847	22,560	II–D
	Total	..	46,041	..	..	..
	% of U.S. total	..	2·69	..	..	..
	KENTUCKY					
86	Poole Consolidated	1943	1,006	1,662	..	..
87	Smith Mills	1942	1,064	6,215	..	..
88	Uniontown	1942	3,091	5,483	..	..
	Total	..	5,161	..	..	..
	% of U.S. total	..	0·30	..	..	..
	LOUISIANA					
	North Louisiana					
89	Caddo	1905	1,913	171,532	18,468	(40)
90	Cotton Valley	1937	2,430	49,459	35,541	II–E, IV
91	Delhi	1945	1,024	1,024	14,976	II–E
92	Haynesville	1921	2,379	87,977	37,023	II–E
93	Holly Ridge	1943	1,430	2,287	27,713	II–E
94	Lake St. John	1942–4	1,800	2,807	47,193	II–E, IV
95	Nebo	1940	3,122	14,178	20,822	II–E, IV
96	Olla	1940	2,906	19,626	25,374	II–E, IV
97	Rodessa	1930	2,528	86,272	18,728	II–E
	South Louisiana					
98	Anse La Butte	1902	2,436	12,340	23,660	II–E, IV
99	Barataria	1939	1,335	6,115	13,885	II–E
100	Bayou Sale	1941	2,878	8,988	41,112	II–E
101	Caillou Island	1930	1,889	39,377	20,623	II–E, IV
102	Delta Farms	1940	3,295	3,482	36,518	II–E
103	Eola	1939	2,476	20,683	19,317	II–E, IV
104	Erath	1940	6,318	11,003	88,997	II–E
105	Gibson, E. and NE.	1937	3,360	16,017	18,983	II–E
106	Golden Meadow	1938	2,484	22,978	27,022	II–E, IV, VI, IX
107	Grand Bay	1938	2,991	14,003	18,997	II–E
108	Gueydan, and W.	1932–45	2,042	8,844	16,156	IV (18)
109	Hackberry, E.	1927	1,615	35,087	19,913	II–E, IV
110	Hackberry, W.	1927	2,150	16,218	23,782	IV
111	Iberia	1917	2,136	34,335	35,665	..
112	Iowa	1931	2,726	57,708	22,292	IV (40, 18)

* Reference (1).

† Reference (29). Data in thousands of barrels.

‡ Roman numerals refer to tables in this article, Arabic numerals are reference numbers in bibliography to articles in Vol. II of this treatise.

TABLE I (*cont.*)

Item No. (1)	STATE *Field* (2)	*Discovery Year** (3)	*Annual production†*		*Estimated reserves†* (6)	*Analytical Tables‡* (7)
			1945 (4)	*Cumulative* (5)		
	LOUISIANA (*cont.*)					
113	Jennings	1901	2,443	89,422	20,578	IV, VI, VII, IX (18)
114	Lafitte	1935	3,997	44,136	50,864	II–E, IV
115	Lake Salvadore	1940	1,544	5,478	14,522	II–E
116	Leeville	1931	1,538	28,362	16,638	IV (18)
117	Neale	1940	2,307	8,052	26,948	II–D
118	No. Crowley	1937	1,657	11,611	14,389	..
119	Paradis	1937	3,542	15,227	54,773	II–E
120	Pine Prairie	1941	1,930	6,434	10,566	II–E
121	Port Barre	1929	1,000	14,251	15,749	IV (18)
122	Quarantine Bay	1937	2,937	15,504	19,496	II–E
123	St. Gabriel	1941	1,909	7,479	12,521	II–E
124	Tepetate, and N.	1935–8	918	14,275	10,725	II–E, IV, VI
125	Tepetate, W.	1944	1,001	1,023	..	..
126	University	1938	1,962	19,189	15,811	IV
127	Venice	1937	3,283	13,253	26,747	IV
128	Ville Platte	1937	2,541	31,847	38,153	II–E, IV, VI
129	Vinton	1910	2,671	48,809	16,191	IV, VI (18)
130	White Lake, E.	1937	1,190	3,096	11,904	II–E
	Total	..	98,033	..	..	..
	% of U.S. total	..	5·73	..	..	..
	MICHIGAN					
131	Deep River	1944	1,475	2,210	7,800	..
132	Fork	1942	1,574	3,867	4,403	II–J
133	Reed City	1941	4,228	29,053	15,140	II–J
	Total	..	7,277	..	..	..
	% of U.S. total	..	0·43	..	..	..
	MISSISSIPPI					
134	Cranfield	1943–4	2,105	2,643	94,407	II–J
135	Eucutta	1943	2,070	2,526	17,474	II–J
136	Heidelberg, and W.	1944	2,889	4,330	80,670	II–J
137	Pickens	1940	2,097	6,631	29,369	II–J
138	Tinsley	1939	9,345	86,164	39,380	II–J
	Total	..	18,506	..	..	..
	% of U.S. total	..	1·08	..	..	..
	MONTANA					
139	Cut Bank	1926	4,907	47,196	53,977	II–J, IV, VI
140	Elk Basin	1915–43	947	2,916	14,113	..
141	Kevin-Sunburst	1922	1,936	47,232	19,721	II–J, IV
	Total	..	7,790	..	..	..
	% of U.S. total	..	0·46	..	..	..
	NEBRASKA					
142	Falls City	1939	258	3,989	..	II–J
	% of U.S. total	..	·02	..	..	..
	NEW MEXICO					
143	Arrowhead	1938	1,839	9,755	20,245	II–F
144	Eunice	1928	5,707	77,143	72,857	II–F, IV
145	Grayburg-Jackson	1936	1,952	17,447	22,553	II–F, IV
146	Hobbs	1928	3,874	112,700	62,300	IV (40)
147	Loco Hills	1939	993	9,931	16,069	II–F, IV
148	Maljamar, and N. and S.	1926–40	2,085	11,858	..	II–F, IV
149	Monument	1934	7,139	73,927	101,073	II–F, IV, VI, VII, X
150	Square Lake	1941	1,008	3,530	17,470	II–F, IV
151	Vacuum	1929	4,585	31,107	98,893	II–F, IV
	Total	..	29,182	..	..	..
	% of U.S. total	..	1·70	..	..	..
	OKLAHOMA					
152	Apache	1941	2,308	8,820	16,180	II–G
153	Burbank	1920	3,128	218,039	31,969	VI (40)
154	Burbank, S.	1926–34	2,370	41,017	28,983	II–G
155	Cement	1917	5,165	38,072	21,928	II–G, VI
156	Crescent	1933	1,845	18,016	11,984	II–G
157	Cumberland	1940	4,119	17,830	42,170	II–G
158	Cushing	1912	2,814	371,156	28,744	II–G
159	Earlsboro	1926	1,737	187,746	12,254	(40)
160	Edmond, W.	1943	26,548	34,753	145,247	II–G, IV
161	Fitts	1933	1,701	102,248	12,752	II–G

* Reference (1).

† Reference (29). Data in thousands of barrels.

‡ Roman numerals refer to tables in this article, Arabic numerals are reference numbers in bibliography to articles in Vol. II of this treatise.

TABLE I (*cont.*)

Item No. (1)	STATE *Field* (2)	*Discovery Year** (3)	*Annual production*† *1945* (4)	*Cumulative* (5)	*Estimated reserves*† (6)	*Analytical Tables*‡ (7)
	OKLAHOMA (*cont.*)					
162	Glenn	1905	2,359	228,308	21,692	II–G
163	Healdton	1913	2,423	200,918	24,088	IV (40)
164	Oklahoma City	1928	12,968	631,882	68,118	IV, VI, VII, XI (40)
165	Pauls Valley	1942	3,181	9,907	13,093	II–G
166	Pauls Valley, E.	1944	1,264	1,506	5,494	II–G
167	Seminole	1926	1,990	160,304	14,696	(40)
168	St. Louis	1927	1,703	167,345	12,655	VI (40)
169	Tatums-Tussey	1933	1,457	26,775	10,225	II–G
	Total	..	79,080	..	..	..
	% of U.S. total	..	4·62	..	..	..
	PENNSYLVANIA					
170	Bradford	1871	11,096 (1944)	..	..	II–J
	% of U.S. total	..	0·65	..	..	..
	TEXAS					
	East Texas					
171	Cayuga	1934	2,594	37,099	32,406	II–H, V
172	East Texas	1930	131,210	2,226,504	2,673,496	V, VI, VII, XII (40)
173	Hawkins	1940	12,210	46,666	159,334	II–H, V, VI
174	Long Lake, and E.	1933	1,962	18,253	29,538	V
175	New Hope	1943	1,596	2,722	18,578	II–H
176	Quitman	1942	2,130	4,853	21,147	II–H
177	Sulfur Bluff	1936	1,350	13,854	19,950	II–H
178	Talco	1936	8,284	83,805	84,716	II–H
179	Van	1929	10,494	161,597	290,506	(40)
	Upper Texas Gulf Coast					
180	Amelia	1936	1,484	11,936	13,064	II–H, V
181	Anahuac	1935	10,923	55,378	219,622	V (18)
182	Barbers Hill	1916	1,927	83,315	26,685	V, VI (18)
183	Bay City	1934	1,404	9,664	10,336	II–H, V, VI
184	Clear Lake	1938	1,362	6,452	14,548	II–H, V
185	Conroe	1931	20,992	206,155	493,845	V, VI, VII, XIII (40, 18)
186	Esperson	1929	1,031	11,257	12,743	V (18)
187	Fairbanks	1938	2,561	19,392	20,608	II–H, V
188	Fannett	1927	2,660	9,138	10,862	V (18)
189	Fig Ridge	1940	2,817	6,404	28,596	..
190	Ganado	1941	1,170	4,120	15,880	..
191	Gillock	1935	1,331	12,511	12,489	..
192	Hastings	1934	20,608	106,295	268,705	V, VI, VII, XIII (18)
193	Hull	1918	1,489	101,053	13,947	V (18)
194	Lolita	1940	2,214	10,192	24,808	II–H, V
195	Lovell's Lake	1938	1,645	9,871	20,129	II–H, V
196	Manvel	1931	2,827	31,777	28,233	V (18)
197	Markham, N.	1941	1,514	9,820	15,180	..
198	Old Ocean	1934	5,936	34,846	165,154	II–H, V, VI, VII, XIII
199	Racoon Bend	1934	3,330	35,110	29,890	V (18)
200	Segno	1936–8	1,323	10,848	11,152	II–H, V, VI, XIII
201	South Houston	1935	1,756	12,608	14,392	V (18)
202	Stowell	1941	6,237	12,822	42,178	..
203	Sugarland	1928	2,466	38,601	51,399	V (18)
204	Thompson	1931	12,749	85,050	189,950	II–H, V
205	Tomball	1933	3,653	33,573	31,427	V (18)
206	Webster	1937	19,820	64,512	285,488	II–A, V
207	West Columbia	1902	2,626	98,549	26,441	V (18)
208	West Ranch	1938	7,127	33,140	201,860	II–H, V
209	Withers, N.	1936	4,311	12,483	27,517	II–H
	Lower Texas Gulf Coast					
210	Agua Dulce	1928	7,608	22,430	102,570	II–H
211	Aransas Pass	1936	1,318	15,048	11,012	II–H, V
212	Flour Bluff	1936	1,386	11,533	14,467	(18)
213	Greta	1933	3,171	36,754	23,246	(18)
214	Heyser	1936	2,778	26,606	23,394	V (18)
215	Kelsey	1938	1,136	4,563	14,437	II–H, V
216	La Rosa	1938	1,413	7,402	12,598	II–H, V, VI
217	McFaddin	1930	1,641	9,114	10,886	(18)
218	Placedo	1935	1,741	18,622	16,378	V (18)
219	Plymouth	1935	3,148	35,837	29,167	V, VI, VII, XIV (18)
220	Refugio	1922	1,905	49,581	25,419	V (18)
221	Richard King	1937	1,172	5,271	10,729	..
222	Saxet (deep)	1937	1,839	60,589	14,411	V, VI, XIV (18)

* Reference (1). † Reference (29). Data in thousands of barrels.

‡ Roman numerals refer to tables in this article, Arabic numerals are reference numbers in bibliography to articles in Vol. II of this treatise.

TABLE I (*cont.*)

Item No. (1)	STATE *Field* (2)	*Discovery Year** (3)	*Annual production†*		*Estimated reserves†* (6)	*Analytical Tables‡* (7)
			1945 (4)	*Cumulative* (5)		
	TEXAS (*cont.*)					
223	Seeligson	1939	11,384	21,322	378,672	II–H
224	Tom O'Connor	1934	17,676	83,103	366,897	V, VI, VII, XIV (18)
225	White Point, East	1938	4,423	24,006	40,994	V
226	Willemar	1940	2,783	4,241	31,759	..
	South and South Central Texas					
227	Benevides	1937	1,274	15,336	11,664	V
228	Conoco Driscoll	1924	1,017	7,897	12,103	II–H, V
229	Darst Creek	1928	3,139	62,346	17,121	II–H
230	Government Wells	1928	2,282	56,871	28,129	(18)
231	Hoffman	1933	1,300	13,254	11,746	II–H, V
232	Loma Novia	1934	1,087	30,847	14,153	(18)
233	Luling-Branyon	1921	1,563	86,546	21,882	V (40)
234	Rincon, and N.	1938	2,942	12,015	32,885	V, VI
235	Seven Sisters	1934	2,391	24,332	20,668	II–H
236	Sun, and N.	1938	1,597	5,583	14,417	II–H, V
	North and West Central Texas					
237	Hildreth	1942	2,160	3,555	21,445	..
238	Hull-Silk-Sikes	1939	3,975	23,351	39,135	II–H, V, VI, VII, XV
239	KMA	1931	8,309	75,479	79,521	II–H, V, VI, VII
240	Walnut Bend	1938	2,519	11,412	13,588	II–H
	West Texas					
241	Barnhart	1941	1,643	2,924	27,076	II–H
242	Big Lake	1923	1,407	102,799	14,201	V, VI (40)
243	Cowden, N. and deep	1930	9,997	47,215	117,785	II–H, V, VI
244	Cowden, S.	1933	1,358	6,403	13,597	..
245	Embar	1942	1,457	3,475	16,525	II–H
246	Emma	1937	1,010	3,472	15,528	..
247	Foster	1936	6,068	30,290	47,710	II–H, V, VI
248	Fuhrman-Mascho	1930	1,662	6,682	23,318	II–H, V
249	Fullerton	1942	6,478	9,745	190,255	II–H
250	Goldsmith	1934	8,381	63,601	181,399	II–H, V, VI
251	Hendrick	1926	1,555	209,712	15,288	V (40)
252	Howard-Glasscock	1926	4,948	118,877	56,213	II–H, V, VI
253	Iatan-E. Howard	1926	1,595	20,748	19,252	II–H, V, VI
254	Johnson	1935	1,368	5,422	24,588	..
255	Jordan	1937	2,274	12,055	27,945	II–H
256	Keystone	1930	6,535	20,198	339,802	II–H
257	McCamey	1925	3,199	64,133	45,867	II–H, V
258	McElroy	1926	10,717	154,311	95,689	II–H, V, VI
259	Mabee	1943	1,038	1,396	23,604	..
260	Means	1934	1,225	9,369	55,631	II–H
261	Penwell	1930	1,133	26,530	13,470	II–H
262	Seminole	1937	8,088	25,063	104,937	II–H, V
263	Slaughter	1936	23,440	72,299	407,701	II–H, V, VI, VII, XVI, XVII
264	Waddell	1927	1,403	7,893	42,107	II–H
265	Ward, No.-Estes	1929–36	4,622	52,283	47,717	II–H, V
266	Wasson	1936	23,256	102,160	477,840	II–H, V, VI, VII, XVI
267	Yates	1926	13,053	300,880	339,120	V, VI, VII, XVII (40)
	Texas Panhandle					
268	Carson County	1921	4,552	55,525	54,475	..
269	Gray County	1925	14,880	246,569	213,331	(40)
270	Hutchinson County	1922	10,872	200,412	109,588	(40)
	Total	..	604,414	..	..	..
	% of U.S. total	..	35·30	..	..	..
	WYOMING					
271	Byron	1918–30	2,429	13,943	16,940	II–I
272	Elk Basin (black)	1942	3,048	19,820	151,180	II–I, XVIII, XIX
273	Frannie	1928	1,518	10,299	11,140	II–I
274	Hamilton Dome	1918	1,041	34,121	18,959	II–I
275	Lance Creek	1918–37	5,463	69,123	43,560	II–I, IV, VI
276	Lost Soldier	1916–30	1,525	29,821	33,475	II–I, IV
277	Oregon Basin, N.	1912–27	4,394	34,521	122,905	II–I
278	Salt Creek (light)	1906	4,499	317,664	53,900	II–I, IV, VI
279	Wertz	1920–35	1,460	11,746	17,520	II–I
	Total	..	25,377	..	..	..
	% of U.S. total	..	1·48	..	..	..
	Grand total 1945 production	..	1,307,084	..	..	..
	% of U.S. total	..	76·35	..	..	..

---

* Reference (1).

† Reference (29). Data in thousands of barrels.

‡ Roman numerals refer to tables in this article, Arabic numerals are reference numbers in bibliography to articles in Vol. II of this treatise.

Item (1)	Field (2)	icat-	Viscous lubricating dist.		Total dist. % (24)	Residuum			Carbon residue of crude % (28)	Base of crude (29)	Indication of wax (30)	Bibli. ref. (31)
		zv. PI. 1)	% (22)	Grav. °API. (23)		% (25)	Grav. °API. (26)	Carbon residue % (27)				
II–A.	ARKANSAS											
1	Atlanta	30·6	..	..	84·9	14·6	23·5	2·6	0·4	Paraffin	Present	8
2	Magnolia	25·6	..	..	76·8	22·4	17·8	6·9	1·5	Intermediate	,,	8
3	McKamie	32·3	..	..	83·0	13·7	22·6	5·9	0·8	Paraffin	,,	..
4	Midway	24·2	..	..	73·0	24·9	13·6	11·3	2·8	Intermediate	,,	..
5	Schuler	24·9	..	..	69·3	30·2	14·1	10·2	3·1	,,	,,	8
7	Stephens	24·7	..	..	64·0	34·5	9·6	18·5	7·3	,,	,,	..
II–B.	CALIFORNIA											
	San Joaquin Valley Fi											
8	Antelope Hills	17·6	15·4	17·6–14·7	47·8	49·2	7·8	14·0	6·9	Naphthene	Absent	..
12	Canal	24·3	4·1	24·3–22·5	72·8	24·4	12·9	11·9	2·9	,,	Present	..
14	Coalinga-Guijarral Hills	23·5	1·9	23·5–22·8	74·1	23·0	13·9	9·4	2·2	Intermediate	Absent	..
16	Coles Levee, No.	23·1	7·1	23·1–19·7	72·9	23·4	11·6	12·8	3·0	,,	,,	..
20	Greeley	23·8	0·8	23·8–23·5	75·1	22·7	14·7	9·5	2·2	,,	,,	24
29	Paloma	25·6	1·2	25·6–24·0	92·9	2·5	21·6	1·8	0·1	,,	,,	..
30	Pleasant Valley	24·0	4·1	24·0–22·6	66·0	32·5	11·1	13·8	4·5	,,	,,	..
31	Rio Bravo	24·2	1·1	24·2–23·7	80·4	17·9	14·7	9·0	1·6	,,	,,	..
32	Riverdale	24·3	3·1	24·3–23·0	75·7	21·7	12·3	10·9	2·4	,,	,,	..
34	Ten Section	23·3	3·6	23·3–22·0	73·6	21·3	11·7	12·4	2·6	,,	,,	24
	Coastal Fields											
35	Aliso Canyon	20·0	7·8	20·0–17·9	71·7	28·3	8·5	18·2	5·2	Naphthene	,,	..
37	Del Valle	23·3	4·7	23·3–21·5	74·6	23·9	9·4	15·5	3·7	Intermediate	,,	..
40	Newhall-Potrero	23·5	3·1	23·5–22·0	71·4	27·3	12·2	14·4	3·9	,,	,,	..
41	Padre Canyon	24·0	4·2	24·0–22·3	68·0	31·1	10·6	14·3	4·4	,,	,,	..
	Los Angeles Basin Fie											
61	Wilmington	21·5	8·1	21·5–18·6	61·5	36·2	9·0	9·0	3·3	Naphthene	,,	24
II–C.	ILLINOIS											
65	Bridgeport	24·5	6·9	24·5–23·0	73·8	24·5	15·0	10·7	2·6	Intermediate	Present	..
66	Centralia	27·0	..	..	73·9	25·1	15·1	12·5	3·1	,,	,,	..
67	Clay City, Cons.	26·8	..	..	72·2	25·1	18·2	8·4	2·1	,,	,,	32
69	Louden	25·4	0·3	25·4–25·2	73·5	24·4	16·2	10·8	2·6	,,	,,	..
70	New Harmony	24·7	..	..	73·2	23·2	14·7	9·6	2·2	,,	,,	32
71	Noble	27·1	..	..	72·3	24·2	18·4	8·2	2·0	,,	,,	32
72	Robinson	26·4	..	..	71·4	28·3	17·1	7·6	2·2	,,	,,	..
73	Salem	26·8	0·6	26·8–26·4	74·3	25·0	17·1	9·6	2·4	,,	,,	..
II–D.	KANSAS											
75	Bemis-Shutts	26·3	1·8	26·3–25·6	71·3	27·2	15·4	12·5	3·4	Intermediate	Present	26
76	Bloomer	27·0	..	..	80·5	18·5	17·1	9·7	1·8	Paraff.-inter.	,,	26
77	Burnett	26·1	1·8	26·1–25·6	67·7	31·3	14·7	13·1	4·1	Intermediate	,,	26
78	Chase	27·1	3·5	27·1–25·0	86·1	10·1	14·7	12·9	1·3	Paraff.-inter.	,,	26
79	Geneseo	25·9	..	..	69·9	26·4	13·8	15·4	4·1	Intermediate	,,	26
80	Gorham	26·6	1·9	26·6–25·9	73·1	25·4	13·9	14·1	3·6	,,	,,	26
74	Grimm	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	,,	[illegible]
	Michigan											
132	Fork	29·7	..	..	84·2	11·8	24·0	2·8	0·3	Paraffin	,,	..
133	Reed City	25·7	..	..	82·4	13·6	19·2	5·4	0·7	Paraff.-inter.	,,	..
	Mississippi											
134	Cranfield	28·4	..	..	79·4	18·7	20·8	3·8	0·7	Intermediate	,,	..
135	Eucutta	22·5	..	..	49·0	49·7	2·2	25·7	12·8	Paraff.-inter.	,,	..
136	Heidelberg, and W.	22·5	..	..	52·3	46·8	9·7	16·7	7·8	Intermediate	,,	..
137	Pickens	25·2	..	..	83·9	15·9	20·7	4·8	0·8	Paraff.-inter.	,,	..
138	Tinsley	26·1	..	..	69·0	30·3	13·3	16·3	4·9	,,	,,	..
	Montana											
139	Cut Bank	24·0	0·7	24·0–23·8	78·5	19·1	14·1	9·2	2·0	Intermediate		..
141	Kevin-Sunburst	24·0	..	..	78·3	..	..	6·4	..	,,	,,	43
	Nebraska											
142	Falls City	27·5	..	..	61·8	38·0	16·5	10·4	4·0	Paraff.-inter.	,,	..
	Pennsylvania											
170	Bradford	29·9	..	..	76·7	21·3	26·6	1·9	0·4	Paraffin	,,	25

The data in columns 2–30, inclusive, are adequately explained by the column headings or by table footnotes, with the possible exception of the information in column 29 on the 'base of crude'. Kraemer [18, 1938] discusses this property, and it seems unnecessary to repeat it here. However, it should be emphasized that this method of classification is empirical and may be misleading unless used in conjunction with other data. For example, the crude oil from the Eucutta field, Mississippi, item 135, is classed as paraffin-intermediate in base, yet contains 49·0% of residuum (A.P.I. gravity, 2·2°). This is at wide variance with the crude oil from the Golden Meadow field, Louisiana, item 106, which has the same classification but contains only 17·1% of residuum (A.P.I. gravity, 22·8°). The Bureau of Mines, although still reporting these classifications, has recognized the inherent weaknesses of the system. These are discussed in Technical Paper 610 [33, 1940], which proposes an index number for individual distillation fractions as a partial solution.

Tables III, IV, and V. As a result of war work conducted during 1941–5, the Bureau of Mines accumulated a considerable amount of data relating to the crude oils of the United States as sources of 'base stock' for use in the manufacture of aviation gasoline. Some of these data are given in Tables III, IV, and V for crude oils from California, the Mid-Continent area, and Texas, respectively. In column 1 the item numbers refer to the same items in Tables I and II, and in column 2 the fields are listed alphabetically by States and fields.

For most of the oils the A.P.I. gravities given in column 3 agree fairly well with those in Table II. The data in the two tables, however, frequently were obtained from analyses of different samples; therefore there is some variation, especially for fields where there are several producing horizons, as the samples reported in Tables III, IV, and V generally represent average production. The percentage of 'base stock' in each crude oil is shown in column 4 and the properties of the 'base stocks' in columns 5 to 12, inclusive. In these tabulations no attempt has been made to segregate the 'base stocks' into various grades of usefulness. The data are given primarily to indicate the types of distillate that given crude oils will produce for the specified boiling-range.

The distillates were prepared in 5- to 15-gallon batch stills, each having a column packed with wire helices, equivalent to about 15 theoretical plates, and usually were not treated prior to engine testing. On certain oils desulphurization experiments were made. In general, the distillates were cut in several fractions of successive boiling-range, which were blended successively to give a final product (base stock) having an octane number with 4 ml. of tetraethyl lead of 89·5 to 90·5 by the lean-mixture aviation-gasoline test method A.S.T.M. D614–44 [2, 1944] or until the maximum permissible distillation range of the blend was reached. Of course, all crude oils would not furnish a 'base stock' having such a high octane number, as the tabulated data show. Although most samples were depentanized by discarding the distillate below 100° F., in some of the early work this was not done, and the 'base stocks' have vapour pressures higher than is usually desirable.

The Bureau of Mines, in searching for sources of good 'base stock', tried the effect of catalytic desulphurization over bauxite on a number of distillates from high-sulphur crude oils. Tables IV and V contain some data on 'base stock' obtained both before and after such treatment. The very valuable effects obtained in some instances are clearly demonstrated. This work has been described in more detail by Guthrie and Simmons [17, 1943].

Table VI. Also in connexion with war-time research, the Bureau of Mines determined the toluene and 7-carbon-atom-naphthene contents of a number of crude oils. As such data bear directly on the characteristics of the volatile distillates, these data are summarized in Table VI. As in the previous tables, column 1 gives the item numbers, column 2 the States and fields from which the samples originated, and columns 3 and 4 the volume percentages of toluene and 7-carbon-atom naphthenes in the crude oils. These data were determined by special fractionation of the naphthas from these crude oils, followed by refractive index and density determinations on the fractions. Thorne, Murphy, and Ball [39, 1945] have described the method used for determining aromatic hydrocarbons, and Gooding, Adams, and Rall [15, 1946] the general analytical method applicable to these determinations.

Table VII. The application of the analytical method described by Gooding *et al.* [15, 1946] to nine naphthas in the boiling-range 97° to 243° F. is of considerable interest as characteristic of the volatile portions of certain crude oils. Table VII presents the estimated content of the individual hydrocarbons in the boiling-range indicated.

Characteristics of United States Crude Oils

Alabama. The only producing field in Alabama (1946) is the Gilbertown field, near the Mississippi boundary, which produced 187,000 bbl. in 1945. The oil has a sulphur content of more than 4%, and contains about 50% of asphalt. The distillate is paraffinic through the kerosine range, but as the distillation proceeds, rapidly becomes increasingly naphthenic or aromatic. In many respects it resembles item 135, oil from the Eucutta field in Mississippi, but is not as viscous.

Arkansas. The State of Arkansas produced 1·67% of the country's petroleum in 1945 and has an estimated reserve of 1·3%. The seven fields given in Table I represent 1·22% of the total U.S. production and 0·92% of its reserves. Analyses for six of these fields are given in Table II. A.

In 1940 the Bureau of Mines published [8] detailed analyses of 45 samples of crude oil from Arkansas and pointed out that a predominant characteristic of Arkansas crude oils is their high content of sulphur. Of the 45 samples, 35 had a sulphur content of 0·7% or more, and the average for all was 1·51%. In general, other characteristics show variations that are proportional to some degree with the sulphur content; thus the A.P.I. gravity, the percentage of gasoline naphtha, the A.P.I. gravity of the distillates, and the residuum, all decrease with increase in sulphur, while the percentage of residuum, carbon residue, and viscosity of the distillates increase with increase in sulphur content. The data in Table II. A accord with these conclusions as applied to Arkansas oils, but such conclusions cannot be applied to all oils or over wide areas.

California. California produced 19·04% of the total U.S. output in 1945 and had reserves estimated at 16·3% of the U.S. total. The California fields listed in Table I account for 18·37% of the 1945 U.S. production and represent reserves of 15·7%.

Merrill [27, 1938] gives a very good description of California crude oils through 1935; consequently, only important discoveries since that date are listed in Table II. B. The most important fields discovered since 1935 are Coalinga–Guijarral Hills (item 14), Coles Levee, North (item 16), Greeley (item 20), Rio Bravo (item 31), and Ten

TABLE III

Aviation Base Stock Data for California Crude Oils

	Crude-oil source and gravity			*Aviation base stock*							
				*Aviation octane number** *Tetraethyl lead, ml.*			*Distillation†* *°F at % evap.*				
Item No. (1)	*Field* (2)	*°API* (3)	*% of crude oil* (4)	0 (5)	1·5 (6)	4 (7)	10 (8)	50 (9)	90 (10)	*RVP‡ lb.* (11)	*Sulphur wt. %* (12)
	San Joaquin Valley Fields										
9	Belridge, No.	37·2	17·7	68·9	83·9	89·5	160	193	221	5·4	0·006
10	Belridge, So.	18·1	2·7	. .	. .	84·6	. .	. .	. .	. .	. .
14	Coalinga-Guijarral Hills	29·3	13·4	69·9	84·5	91·1	158	205	244	5·8	0·007
18	Elk Hills	22·5	6·2	74·5	86·3	91·4	200	228	261	2·8	0·012
20	Greeley	39·0	24·9	68·3	82·7	89·7	140	205	255	7·1	0·006
23	Kettleman No. Dome	38·2	16·7	69·4	85·8	92·1	132	174	203	8·5	0·006
26	Midway-Sunset	21·0	9·3	73·0	85·2	91·4	180	228	263	3·0	0·010
27	Mountain View	25·6	8·4	71·6	86·0	91·1	168	213	250	4·6	0·008
31	Rio Bravo	38·8	17·1	71·6	86·5	92·3	127	170	203	9·8	0·010
32	Riverdale	38·2	22·2	65·8	. .	87·7	151	195	239	6·2	0·003
34	Ten Section	36·6	24·3	69·2	82·9	90·5	138	202	251	7·8	0·008
	Coastal Fields										
36	Capitan	24·0	8·0	68·9	82·0	89·8	204	235	282	1·9	0·009
42	Rincon	30·4	13·2	69·8	84·7	91·0	155	192	225	5·8	0·007
43	San Miguelito	32·8	21·5	69·7	. .	92·0	135	202	253	8·5	0·009
45	Santa Maria Valley	14·8	7·6	<65	. .	86·6	157	204	244	5·6	0·009
46	Ventura Avenue	31·0	41·5	71·9	87·2	92·3	135	184	216	9·2	0·006
	Los Angeles Basin Fields										
48	Brea Olinda	21·5	6·8	71·0	82·7	90·1	182	220	258	3·4	0·018
49	Coyote, East	23·0	11·3	71·4	86·1	90·0	183	230	271	3·1	0·019
50	Coyote, West	28·2	10·3	70·1	84·1	90·3	165	200	243	4·7	0·011
51	Dominguez	30·0	12·0	69·9	83·5	91·4	156	195	231	6·3	0·013
52	Huntington Beach	23·0	8·1	71·7	82·4	90·4	154	208	257	7·0	0·030
53	Inglewood	27·3	11·7	70·8	82·4	89·5	180	216	250	3·8	0·016
54	Long Beach	25·2	6·2	. .	. .	90·5	154	193	224	6·1	0·013
55	Montebello	32·7	17·1	70·0	83·9	89·5	167	208	246	5·0	0·008
57	Rosecrans	32·5	10·8	71·9	85·8	91·4	155	184	210	5·7	0·008
58	Santa Fe Springs	33·4	11·2	72·3	86·6	91·4	140	183	212	7·6	0·009
59	Seal Beach	27·0	7·6	73·2	86·1	91·9	151	190	220	6·4	0·015
60	Torrance	23·0	7·3	73·6	. .	91·9	131	184	228	8·8	0·021
61	Wilmington	21·6	6·5	71·7	85·1	91·7	161	201	241	6·1	0·017

* Reference (2). † Reference (3). ‡ Reference (4).

TABLE IV

Aviation Base Stock Data for Mid-Continent Crude Oils

	Crude-oil source and gravity			*Aviation base stock*							
				*Aviation octane number** *Tetraethyl lead, ml.*			*Distillation†* *°F at % evap.*				
Item No. (1)	*Field* (2)	*°API* (3)	*% of crude oil* (4)	0 (5)	1·5 (6)	4 (7)	10 (8)	50 (9)	90 (10)	*RVP‡* *lb.* (11)	*Sulphur wt. %* (12)
	ARKANSAS										
6	Smackover	20·7	3·7	73·2	86·1	90·7	172	208	242	4·1	0·023
	ILLINOIS										
69*a*	Louden (Devonian) . .	28·8	7·6	76·8	86·6	92·4	197	244	266	4·4	0·022
	LOUISIANA										
90	Cotton Valley . . .	45·2	10·3	..	..	92·0	123	151	180	10·0	0·005
94	Lake St. John . . .	33·2	13·0	73·3	87·2	92·0	164	229	275	6·1	0·003
95	Nebo	38·8	9·4	68·9	..	91·3	147	180	203	6·6	0·007
96	Olla	31·3	6·0	72·6	86·3	92·2	202	225	260	2·2	0·013
98	Anse La Butte . . .	37·8	15·5	64·5	79·0	87·3	160	204	242	6·8	0·001
101	Caillou Island . . .	36·0	7·8	71·5	84·8	91·1	164	197	228	5·1	0·012
103	Eola	45·2	19·2	67·7	..	92·3	122	182	224	10·7	0·008
106	Golden Meadows	37·6	5·4	67·0	81·6	90·0	144	182	218	7·5	0·004
108	Gueydan, and W. . . .	39·2	11·6	74·8	87·3	92·3	183	221	259	3·5	0·008
109	Hackberry, E. . . .	26·8	7·2	73·2	85·8	90·8	199	226	269	3·2	0·015
110	Hackberry, W. . . .	29·5	3·2	72·2	..	90·3	148	186	216	7·2	0·008
112	Iowa	37·8	9·2	69·8	..	90·3	149	183	207	7·0	0·008
113	Jennings	38·0	4·3	69·5	..	89·9	152	181	211	6·4	0·006
114	Lafitte	38·2	11·3	61·4	76·4	85·0	172	215	256	5·2	0·000
116	Leeville	30·6	4·3	74·8	..	91·4	150	186	220	6·3	0·021
121	Port Barre	35·8	10·5	70·7	85·5	91·2	140	182	212	7·7	0·005
124	Tepetate	35·8	12·8	69·2	83·9	89·7	149	189	223	6·3	0·009
126	University	35·4	11·2	74·5	87·0	92·2	186	217	255	3·7	0·008
127	Venice	38·8	12·6	67·0	82·4	89·8	131	165	199	9·2	0·005
128	Ville Platte	44·1	20·3	..	..	90·5	138	180	214	8·2	0·008
129	Vinton.	32·5	13·8	70·5	..	89·1	181	220	261	3·8	0·001
	MONTANA										
141	Kevin-Sunburst . . .	31·0	5·8	..	..	91·6	145	175	205	6·2	0·011
139	Cut Bank	37·8	10·0	..	..	88·9	116	159	196	..	..
	NEW MEXICO										
144	Eunice.	33·8	9·1	71·3	..	88·8	128	157	184	8·4	0·040
	„ §	33·0	17·2	67·4	..	88·6	154	199	236	6·8	0·003
145	Grayburg-Jackson. . . .	37·4	18·0	..	..	82·0	145	185	217	7·1	0·085
146	Hobbs.	34·2	19·6	<65	..	79·6	155	201	240	6·9	0·070
	„ §	34·2	19·6	<65	.	85·6	164	204	242	5·6	0·012
147	Loco Hills	36·0	12·5	65·5	..	82·6	145	172	196	6·7	0·083
	„ §	36·0	12·5	64·8	..	88·0	146	172	197	6·6	0·001
148	Maljamar	38·6	11·9	73·5	81·3	88·5	100	144	178	14·1	0·053
149	Monument	31·9	15·6	66·9	..	85·8	148	199	240	7·5	0·047
	„ §	31·9	15·6	..	..	90·6	156	200	241	6·4	0·001
150	Square Lake.	36·6	16·4	65·4	..	87·3	148	195	230	7·2	0·011
	„ §	36·6	16·4	65·9	..	89·6	143	194	232	7·0	0·001
151	Vacuum	38·4	9·7	..	..	89·2	87	126	159	15+	0·005
	OKLAHOMA										
160	Edmond, West	41·9	6·6	..	..	87·6	144	164	181	7·1	0·002
163	Healdton	32·5	5·9	..	..	88·0	144	169	192	7·1	0·016
	„ §	32·5	5·9	..	..	90·6	145	169	192	6·9	0·000
164	Oklahoma City . . .	..	7·0	..	..	86·6	139	177	223	7·0	0·003
	WYOMING										
275	Lance Creek. . . .	44·7	14·8	66·2	84·2	89·5	123	163	195	10·3	0·010
276	Lost Soldier	29·3	5·3	72·1	83·5	89·8	205	242	283	2·1	0·013
278	Salt Creek	37·4	12·1	67·0	82·0	89·5	137	183	219	8·0	0·008

* Reference (2). † Reference (3). ‡ Reference (4). § These distillates were desulfurized over bauxite. See reference (17).

TABLE V. *Aviation Base Stock Data for Texas Crude Oils*

	Crude-oil sources and gravity			*Aviation base stock*							
				Aviation octane number Tetraethyl lead, ml.*			*Distillation† ° Fat % evap.*			*RVP‡ lb.* (11)	*Sulphur wt. %* (12)
Item No. (1)	*Field* (2)	*°API* (3)	*% of crude oil* (4)	0 (5)	1·5 (6)	4 (7)	10 (8)	50 (9)	90 (10)		
	TEXAS										
	East Texas										
171	Cayuga	28·0	13·0	65·1	82·0	90·2	125	170	207	9·0	0·010
172	East Texas	38·8	16·8	67·4	83·9	89·5	138	181	217	7·3	0·009
173	Hawkins	26·8	11·0	..	..	82·7	..	..	..	..	..
174	Long Lake	40·4	13·4	67·0	84·2	89·9	139	178	210	7·5	0·009
	Upper Texas Gulf Coast										
180	Amelia	29·5	9·8	71·3	84·7	89·8	202	226	279	2·2	0·007
181	Anahuac	35·4	7·7	69·4	..	91·0	134	191	221	8·4	0·006
182	Barbers Hill	33·6	12·7	70·1	..	90·1	162	210	251	6·0	0·001
183	Bay City	35·8	7·4	..	..	85·0	164	205	237	5·3	0·001
184	Clear Lake	27·1	4·1	72·3	..	90·6	193	222	259	2·8	0·005
185	Conroe	39·4	17·2	67·1	82·0	89·5	160	204	239	6·4	0·003
186	Esperson	41·1	14·3	70·6	85·3	91·9	133	188	217	9·7	0·005
187	Fairbanks	38·4	10·9	70·8	86·1	91·9	135	181	208	9·0	0·006
188	Fannett	35·0	5·5	66·8	..	89·7	155	202	239	6·2	0·009
192	Hastings	31·5	8·7	70·8	84·6	89·9	176	212	253	3·8	0·009
193	Hull	31·0	9·3	..	..	91·9	163	196	222	5·5	0·006
194	Lolita	33·4	10·5	71·6	84·9	90·9	154	194	227	6·4	0·007
195	Lovell's Lake	38·4	16·9	69·9	83·6	90·5	166	211	249	4·9	0·007
196	Manvel	27·0	2·6	74·9	..	92·2	191	221	268	4·3	0·013
198	Old Ocean	48·1	26·1	67·2	83·2	90·4	150	188	215	6·2	0·007
199	Racoon Bend	33·6	17·4	74·2	85·8	92·0	183	223	261	4·1	0·007
200	Segno	38·0	17·7	70·8	82·8	89·5	166	213	252	5·2	0·008
201	South Houston	25·4	4·6	71·0	85·8	90·9	172	204	239	4·5	0·007
203	Sugarland	28·8	6·6	70·1	..	84·8	167	206	236	5·4	0·061
204	Thompson	25·4	2·5	74·7	..	92·7	189	218	259	3·6	0·008
205	Tomball	41·3	9·0	71·5	86·3	91·4	147	181	205	6·4	0·009
206	Webster	29·3	7·3	71·6	84·3	90·8	180	216	263	3·3	0·010
207	West Columbia	28·9	2·6	69·9	..	89·5	158	188	218	5·8	0·007
208	West Ranch	30·2	9·8	72·0	83·8	89·7	178	215	259	4·6	0·014
	Lower Texas Gulf Coast										
211	Aransas Pass	46·7	8·4	..	..	92·6	136	163	188	8·0	0·005
214	Heyser	32·5	16·9	71·7	85·1	90·5	182	214	253	4·6	0·005
215	Kelsey	45·2	16·1	71·7	82·5	89·8	143	183	206	8·0	0·006
216	La Rosa	42·1	21·0	<65	78·6	82·6	149	197	237	7·6	0·001
218	Placedo	38·6	6·7	68·9	..	90·5	151	182	208	6·3	0·007
219	Plymouth	32·7	17·4	71·5	85·7	92·4	168	207	249	5·2	0·006
220	Refugio	39·4	8·8	..	..	89·8	151	180	208	6·2	0·008
222	Saxet	45·2	25·3	71·3	85·5	92·2	153	176	203	9·4	0·005
224	Tom O'Connor	35·8	18·7	68·9	83·0	89·7	158	205	249	6·4	0·003
225	White Point, East	38·8	22·9	67·7	81·3	89·3	155	205	246	6·8	0·001
	South and South Central Texas										
227	Benevides	43·8	21·0	60·8	78·1	85·0	179	213	247	4·2	0·002
228	Conoco Driscoll	32·7	14·6	73·8	84·0	91·5	203	230	259	1·9	0·008
231	Hoffman	26·8	5·5	..	..	91·9	202	233	267	2·1	0·010
233	Luling	27·9	1·4	..	..	86·7	..	..	..	..	..
234	Rincon	42·8	28·4	69·8	84·4	90·5	160	212	255	5·9	0·007
236	Sun	46·0	12·9	68·2	84·5	90·3	135	174	199	8·3	0·027
	North and West Central Texas										
238	Hull-Silk-Sikes	41·1	14·6	65·6	..	90·3	134	169	198	8·0	0·008
239	KMA	41·1	9·6	69·9	..	91·4	131	155	179	7·8	0·008
	West Texas										
242	Big Lake	38·0	20·5	68·2	..	83·1	146	204	241	7·2	0·045
	„ §	38·0	9·6	..	..	93·6	143	165	193	6·5	0·003
243	Cowden, No.	34·8	12·7	<65	..	84·6	143	172	198	7·1	0·022
	„ §	34·8	12·7	66·5	..	89·4	144	171	197	6·8	0·001
247	Foster	39·8	9·4	66·3	..	80·6	142	169	199	6·8	0·144
	„ §	35·8	9·4	67·3	..	91·9	143	169	199	6·8	0·001
248	Fuhrman	26·1	5·5	..	..	84·2	..	..	..	..	..
250	Goldsmith	37·4	9·7	..	..	85·0	142	165	190	7·1	0·057
	„ §	37·4	9·7	<65	..	88·0	143	165	190	7·0	0·001
251	Hendrick	26·6	2·6	73·8	..	88·5	165	191	217	4·6	0·052
252	Howard-Glasscock	29·3	5·8	75·1	..	90·0	116	145	171	11·4	0·050
253	Iatan-E. Howard	30·8	16·7	65·7	..	83·6	153	199	237	6·4	0·059
	„ §	30·8	16·7	66·8	..	89·0	156	197	233	6·1	0·001
257	McCamey	28·9	10·7	65·7	..	84·6	136	199	239	7·9	0·056
	„ §	28·9	10·7	68·5	..	90·2	143	202	241	7·0	0·002
258	McElroy	31·7	7·2	73·2	81·1	87·6	110	149	184	13·3	0·047
262	Seminole	34·8	10·8	..	..	83·0	..	..	..	..	..
263	Slaughter	31·9	12·0	<65	..	80·0	144	169	195	7·2	0·135
	„ §	31·9	12·0	65·2	..	88·6	145	170	196	6·9	0·004
265	Ward, No.	32·7	5·9	..	..	84·4	..	..	..	..	..
266	Wasson	33·4	20·6	61·3	..	76·3	150	199	242	7·8	0·171
	„ §	33·4	20·6	60·0	..	84·7	157	204	243	6·7	0·003
267	Yates	29·3	11·2	69·7	..	86·0	160	213	250	6·5	0·058
	„ §	29·3	11·2	70·5	..	92·3	161	214	250	6·2	0·003

* Reference (2). † Reference (3). ‡ Reference (4). § These distillates were desulfurized over bauxite. See reference (17).

TABLE VI

Toluene and C_7-Naphthene Content of United States Crude Oil

Item No. (1)	STATE *Field* (2)	% in crude oil	
		Toluene (3)	*C_7-Naphthenes* (4)
	CALIFORNIA		
	San Joaquin Valley Fields		
14	Coalinga-Guijarral Hills	0·59	2·36
16	Coles Levee, No.	0·27	3·76
18	Elk Hills	0·02	0·95
	Los Angeles Basin Fields		
49	Coyote, East	0·26	3·11
50	Coyote, West	0·33	2·25
53	Inglewood (all zones)	0·28	1·99
	„ (Vickers-Machado)	0·01	0·63
55	Montebello (main area)	0·00	0·85
	„ (west area)	0·25	3·93
	ILLINOIS		
66	Centralia	0·11	2·67
69	Louden	0·19	2·77
73	Salem	0·47	2·86
	KANSAS		
75	Bemis	Trace	2·05
77	Burnett	0·00	2·21
83	Silica	0·03	3·24
	LOUISIANA		
	South Louisiana		
106	Golden Meadow	0·18	1·17
113	Jennings	0·70	1·47
124	Tepetate	0·74	2·29
128	Ville Platte	0·59	3·82
129	Vinton	0·24	3·22
	MONTANA		
139	Cut Bank	0·45	1·45
	NEW MEXICO		
	Lea County Composite	0·90	3·07
149	Monument	0·14	2·31
	OKLAHOMA		
153	Burbank	0·09	1·61
155	Cement	0·29	1·51
164	Oklahoma City	0·38	1·55
168	St. Louis	0·21	2·73
	TEXAS		
	East Texas		
172	East Texas	0·27	2·53
173	Hawkins	0·18	0·61
	Upper Gulf Coast		
182	Barbers Hill	0·35	2·85
183	Bay City	0·43	1·37
185	Conroe	1·76	3·11
192	Hastings	0·04	1·85
198	Old Ocean	1·22	5·56
200	Segno	1·02	2·75
216	La Rosa	0·43	3·55
	Lower Gulf Coast		
219	Plymouth	0·22	4·07
222	Saxet	Trace	0·81
224	Tom O'Connor	0·36	3·61
	South and South Central		
234	Rincon	0·84	5·40
	North and West Central		
238	Hull-Silk-Sikes	0·29	3·86
239	KMA (Strown)	0·43	3·82
	West Texas		
242	Big Lake	Trace	4·15
243	Cowden, No.	1·04	2·51
247	Foster	0·80	2·89
250	Goldsmith	0·52	2·49
252	Howard-Glasscock	0·26	2·20
253	Iatan-E. Howard	1·49	2·41
258	McElroy	0·55	2·12
263	Slaughter	1·46	1·97
266	Wasson	1·17	2·52
267	Yates	0·00	1·42
	WYOMING		
275	Lance Creek	0·27	2·18
278	Salt Creek	0·08	0·94

TABLE VII

Volume Per Cent. of Individual Hydrocarbons in the 97° to 243° F. Boiling Range for Several Representative Naphthas

Item No.	14	113	185	192	198	200	222	224	239
Hydrocarbons	*Coalinga*	*Jennings*	*Conroe*	*Hastings*	*Old Ocean*	*Segno*	*Saxet*	*Tom O'Connor*	*KMA Strawn*
n-Pentane*	0·44	1·12	0·33	0·89	0·36	0·55	1·11	None	0·40
Cyclopentane	1·76	0·67	0·96	1·23	0·85	1·08	0·73	1·04	1·25
2,2-Dimethylbutane . .	0·25	0·42	0·39	0·78	0·58	0·74	0·32	0·60	0·16
2,3-Dimethylbutane . .	2·21	2·05	1·46	1·97	1·88	1·94	1·25	2·09	1·74
2-Methylpentane . . .	2·56	3·47	2·89	2·16	5·23	3·71	1·33	4·61	4·39
3-Methylpentane . . .	1·89	1·03	2·09	1·81	3·36	2·22	0·88	2·62	3·80
n-Hexane	7·75	9·15	6·44	5·18	10·18	8·84	2·29	7·76	12·71
Methylcyclopentane . .	10·29	5·01	6·51	7·42	5·42	6·40	5·52	6·70	7·52
2,2-Dimethylpentane 2,4-Dimethylpentane . .	0·51	1·46	0·96	2·55	1·52	1·38	3·51	1·72	0·79
Benzene	2·22	3·61	3·27	0·16	2·28	1·82	None	0·58	0·59
Cyclohexane	7·63	7·13	10·40	13·66	7·30	9·64	15·07	10·94	4·68
1,1-Dimethylcyclopentane .	1·17	1·00	0·35	0·70	0·83	0·59	1·30	0·68	0·45
2,3-Dimethylpentane 2-Methylhexane . .	2·69	6·14	3·45	4·53	6·71	5·32	2·39	5·79	5·81
trans-1,3-Dimethylcyclopentane	4·92	2·53	2·62	5·78	3·87	2·98	4·33	4·36	7·08
trans-1,2-Dimethylcyclopentane	7·05	1·02	1·59	2·35	1·41	1·29	3·12	2·64	5·29
3-Methylhexane . . .	3·30	2·25	1·90	1·49	2·88	2·01	1·25	3·29	3·90
n-Heptane	5·94	8·42	6·90	2·43	10·92	7·96	1·69	4·96	11·32
Methylcyclohexane . . .	14·55	18·07	22·00	32·39	17·20	21·58	37·48	23·02	12·29
Ethylcyclopentane . . .	4·38	2·34	2·03	3·58	3·48	2·70	4·09	3·22	3·65
2,2-Dimethylhexane . .	0·57	2·39	0·71	0·77	1·51	1·27	1·35	1·51	0·93
2,5-Dimethylhexane 2,4-Dimethylhexane . .	0·56	2·13	2·70	2·02	1·04	1·69	2·11	0·33	0·51
Toluene	7·94	12·02	16·19	0·77	5·87	9·61	None	3·39	2·57
Trimethylcyclopentanes† . .	7·23	3·71	3·56	3·05	3·38	2·56	4·42	3·58	4·56
2,3-Dimethylhexane . .	1·30	2·39	0·22	1·33	1·45	1·87	1·66	3·39	2·49
A trimethylcyclopentane† .	0·89	0·47	0·08	1·00	0·49	0·25	2·80	1·18	1·12
Total	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00

* *n*-Pentane boiling below 97·0° F. not included in these figures. † Data taken from reference (15).

Section (item 34) in the San Joaquin Valley area; Del Valle (item 37) and Newhall–Potrero (item 40) in the Coastal area; and Wilmington (item 61) in the Los Angeles Basin area. Of these, Coalinga–Guijarral Hills and Wilmington are by far the most important. The Coalinga oil has a high gravity and a lower sulphur content than much of the earlier production from this district. As shown in Table III, it yields approximately 14% of 91-octane number aviation gasoline with 4 ml. of tetraethyl lead. Its content of toluene, Table IV, 0·59%, is fairly high compared with most crude oils, and the content of 7-carbon-atom naphthenes is about average. The analysis of the 97–243° F. boiling-range naphtha from this oil, Table VII, shows that it contains more than 50% of naphthenes. Table VIII presents another analysis of this naphtha.

TABLE VIII

Comparison of Naphtha Fractions from Coalinga Crude Oil

Boiling-range cut-points, °F.	*Vol. %*		
	Paraffins	*Naphthenes*	*Aromatics*
110–200	38·5	57·2	4·3
200–242	19·0	62·7	18·3
242–285	28·6	53·7	17·7
285–320	28·7	56·3	15·0

The analysis of Wilmington crude oil (Table II. B) represents the higher-gravity oil produced. There is other production in this field (about 17° A.P.I.) that contains no wax. A composite sample representing field production has a gravity of about 21° A.P.I. and yields about 7% of 91-octane number gasoline (Table III).

In general, California crude oils yield aviation 'base stocks', Table III, of 91-octane number, with 4 ml. of tetraethyl lead, but their lead susceptibility is slightly less than for many Mid-Continent and Texas distillates. The 90% evaporated temperature of the 'base stocks' is somewhat higher than for 'base stocks' from many crude oils, but yet a somewhat lower yield is obtained because of the smaller content of volatile fractions.

The toluene content, Table VI, of the crude oils examined is relatively low, while the content of C_7-naphthenes varies widely. Detailed analyses of other California crude oils are given in Bureau of Mines R.I. 3362 [24, 1937].

Colorado. Colorado is at present one of the less important States in crude-oil production, being credited with only 0·28% of the total U.S. 1945 output, and having estimated reserves of 1·0%. The two fields given in Table I represent 0·20% of the 1945 production in the country and 0·91% of the estimated reserves. By far the most important field is Rangely. Production in this field from the Mancos shale dates from 1919, and in 1933 oil was discovered in the Weber sandstone, but it was not until 1944–5 that this producing zone was really developed. It is now the principal producing formation in the field. The oil, Table II. J, is similar to many Mid-Continent 'intermediate-base' crude oils, except for a sulphur content of about 0·7%. Analyses of other Colorado crude oils are given in Bureau of Mines R.I. 3358 [37, 1937].

Florida. Florida's production is negligible at present, but the State is of interest as a potential producing area. The Sunniland field (item 64) is the discovery field and the crude-oil analysis given, Table II. J, represents production from the discovery well. The oil has a high sulphur content, is paraffinic in the volatile portion, but the heavier fractions are naphthenic or aromatic, and the residuum of 40% has an A.P.I. gravity of 30°. The oil contains wax.

Illinois. Illinois produced 4·29% of the Nation's crude oil in 1945 and has an estimated reserve of 1·6% of the U.S. total. The fields listed in Table I represent 2·0% of the total 1945 production and 0·84% of reserves. The crude oils of Illinois show smaller variations in characteristics from field to field than almost any other large producing area. The eight analyses in Table II. C are indicative of this, and represent typical 'intermediate base' crude oils. The production from a Devonian formation in the Louden field is an important exception, as this crude oil is virtually the only one in the State that will yield 91-octane number 'base stock', as shown in Table IV. The toluene content of most of the oils is low to medium, but the content of 7-carbon-atom naphthenes is somewhat on the high side, as shown in Table VI.

Detailed analyses of other Illinois crude oils are given in Bureau of Mines R.I. 3532 [32, 1940] and Illinois State Geological Survey R.I. 88 [30, 1945].

Indiana. Indiana supplied 0·28% of total 1945 production, and its reserves are estimated at only 0·1%. There is only one field, Griffin (item 74), of importance, and this accounted for almost 50% of the State's production. The analysis of this oil, Table II. J, indicates that it is very similar to the Illinois oils just discussed.

Kansas. Kansas has a long history as an oil-producing State. In 1945 it produced 5·64% of the Nation's oil and had an estimated reserve of 3·0% of the total. The fields listed in Table I represent 2·69% of 1945 U.S. production and 1·38% of the estimated reserve. The crude oils of Kansas, as indicated in Table II. D, are largely of the 'intermediate-base' type, with a slightly higher sulphur content than Illinois oils, and yield gasoline that has a slightly higher A.P.I. gravity. They are not suitable sources for aviation gasoline, and have virtually no toluene and a fair to high content of 7-carbon-atom naphthenes (Table VI). Detailed analyses of Kansas crude oils are given by Lane and Garton [23, 1935].

Kentucky. Crude-oil production in Kentucky was only 0·58% of the Nation's 1945 total, and its reserves are estimated as 0·2%. No recent analyses were available. Most of the recent developments have been in western Kentucky, where production is from the same horizons as are common in Illinois, and a composite sample from that area indicates that the oil is similar to Illinois production.

Louisiana. Louisiana is one of the important oil-producing States, as it contributed 8·03% of the U.S. 1945 output and had estimated reserves of 7·1%. The fields listed in Table I represent 5·73% of the total U.S. production and 4·98% of the reserves. Consideration of the crude oils is usually on the basis of production in 'northern' or in 'southern' Louisiana.

In the northern area are found the paraffinic-type crude oils, such as Cotton Valley (item 90) and Rodessa (item 97). Also, as Table II. E shows, there are produced in this area other oils, such as those from the Lake St. John, Nebo, and Olla fields, that yield excellent aviation gasoline stock. These, although generally classed with such oils as those from Illinois and Kansas by a class definition, in fact differ essentially in composition, as illustrated by the data in Table II. E and Table IV. Except for a few fields, such as Haynesville (item 92), the oils are all low in sulphur content.

The southern Louisiana crude oils in Table II. E also would be classified as intermediate or paraffin-intermediate in type, yet they do not conform in character to the interpretation usually accorded these classifications. Many of the oils contain naphthenes in the gasoline fractions in sufficient quantity so that aviation gasoline of 91-octane number with 4 ml. of tetraethyl lead can be readily prepared. The data in Table IV bring out this fact. The gravities of the lubricating fractions also are from one to two degrees, A.P.I., above those of similarly classified oils from Kansas, Illinois, and Oklahoma; the carbon residues are lower, and wax always is present. The above statement applies to the data in Table II. E and varies somewhat from the previous data reported by Kraemer [18, 1938]. The fact that the newer fields are more paraffinic appears to be roughly correlated with stratigraphic occurrence. The data given by Kraemer were for crude oils produced at depths of about 3,000 ft., with only a few at depths of 5,000–7,000 ft., whereas the data in this report are entirely for oils produced from depths of 5,000 to 10,000 ft. These newer oils appear to be better suited for the manufacture of good viscosity-index lubricating oil than the older production. Detailed analyses of Louisiana crude oils are given in Bureau of Mines R.I. 3476 and 4034 [13, 1939; 9, 1947].

The few data available regarding toluene and C_7-naphthene content, Table VI, show considerable variation; some are good sources of toluene. Table VII presents data on the composition of a 97–243° F. boiling-range naphtha prepared from Jennings crude oil. In actual practice the aviation gasoline cut from this crude can be carried advantageously to a high enough boiling-point to include xylenes, which are present in considerable quantity in this oil and double the yield, with improved performance, as shown in Table IV. Comparative data on distillate fractions from two crude oils, Golden Meadow (item 106) and Jennings (item 113), are of interest and are given in Table IX.

TABLE IX

Composition of Naphtha Fractions from Golden Meadow and Jennings Crude Oils

Boiling-range cut-point, °F.	*Paraffins*		*Naphthenes*		*Aromatics*	
	Jennings	*Golden Meadow*	*Jennings*	*Golden Meadow*	*Jennings*	*Golden Meadow*
110–200	55·6	59·5	36·5	38·5	7·9	2·0
200–242	29·4	30·8	47·7	59·5	22·9	9·7
242–285	38·6	32·1	35·6	57·0	25·8	10·9
285–320	47·8	46·7	36·9	40·0	21·3	13·3

Michigan. Crude oil produced in Michigan in 1945 amounted to 1·01% of the U.S. total, and the State is credited with having reserves of 0·4%. The three fields listed in Table I represent 0·43% of 1945 total national production, and 0·13% of the Nation's reserve. Michigan crude oils are ordinarily considered as being paraffinic, and, as Table II. J shows, the crude oils from these fields are no exception. They often contain more sulphur than is usually expected in such paraffinic oils. The gasoline produced from them is of low octane number because of the high content of normal paraffins present, but good solvents and Diesel fuels can be produced by suitable distillation procedures. Detailed analyses of other Michigan crude oils can be found in Bureau of Mines R.I. 3346 [12, 1937].

Mississippi. Crude-oil production in Mississippi in 1945 was 1·11% of the Nation's total and the reserves are estimated at 1·4%. The fields in Table I represent 1·08% of the total U.S. 1945 production and 1·23% of the reserves.

Mississippi crude oils show considerable variation in their characteristics, as the data in Table II. J indicate. They range from a typical high-grade intermediate oil, such as that from the Cranfield field (item 134), with a sulphur content of only 0·13, to a paraffin-intermediate oil from Eucutta (item 135) that has a sulphur content of 4·17 and a *naphthenic* residuum of 50% (gravity 2·2° A.P.I.). In general, the gasoline is too paraffinic to have a good octane number, except that from Cranfield crude oil, which should be good. Some of the oils should be good sources of asphalt in spite of their classification as paraffin intermediates. Wax is present in all these crude oils.

Montana. In 1945 Montana produced 0·50% of the total U.S. crude oil and had reserves estimated at 0·4%. The three fields given in Table I represent 0·46% of the U.S. production for 1945 and 0·42% of the reserves. No important discoveries have been made in Montana for many years, except the Montana extension of the Elk Basin field. The Cut Bank (item 139) and Kevin–Sunburst (item 141) fields produce high-grade intermediate oils, of which the latter is the better from the viewpoint of the octane number of the gasoline (Table IV). The toluene and C_7-naphthene content of Cut Bank oil are given in Table VI. The Elk Basin crude oil is similar to that produced in the Wyoming field of the same name and is discussed there. Detailed analyses of Montana crude oils are given in two Bureau of Mines reports [31, 1928; 37, 1937].

Nebraska. Only one field of any importance has been found in Nebraska—the Falls City field discovered in 1939. An analysis of this oil (item 142) is given in Table II. J. It is classed as a paraffin-intermediate oil, but has a residuum of 38·0% (gravity 10·8° A.P.I.), indicative of a considerable quantity of asphaltic material.

New Mexico. Crude-oil production in New Mexico was 2·20% of the national total for 1945, and the State has reserves estimated as 2·7% of the total for the country. The fields listed in Table I represent 1·70% of the total U.S. production in 1945 and 1·95% of the reserves. Most of the crude oil produced in New Mexico originates in Permian limestone, and the oils are characterized by a high content of sulphur. The sulphur compounds are largely of the aliphatic mercaptan and disulphide type and are therefore susceptible to treating. The oils are all classed as intermediate, and most of them contain wax, as shown in Table II. F. Although desulphurization by passage of the vapours over bauxite at 750° F. will remove virtually all the sulphur and cause marked increase in the leaded octane number, as shown in Table IV, only a few of these oils even then will yield aviation gasoline. References pertaining to this work are [5, 1941] and [17, 1943], and detailed analyses of New Mexico crude oils are given by Lane [21, 1942]. A group hydrocarbon analysis of naphtha from Monument (item 149) crude oil is presented in Table X.

TABLE X

Composition of Naphtha Fractions from Monument Crude Oil

Boiling-range cut-point, °F.	*Composition in volume %*		
	Paraffins	*Naphthenes*	*Aromatics*
110–200	61·6	37·7	0·7
200–242	31·9	63·5	4·6
242–285	32·9	61·6	5·5
285–320	33·0	60·3	6·7

Although the above indicates a relatively small content of aromatics, Table VI shows that a composite crude oil from Lea County has a high content of both toluene and C_7-naphthenes.

Oklahoma. In 1945 Oklahoma produced 8·14% of the Nation's crude oil and had an estimated reserve of 4·8%. The fields given in Table I represent 4·62% of the total U.S. production and 2·48% of the reserves. The major producing areas yield crude oils of the intermediate type, as shown by the data in Table II. G. Some of the oils, such as Burbank (item 154) and to a lesser extent Oklahoma City (item 164) and West Edmond (item 160), are excellent sources of Diesel fuels and lubricating oils. Only a few scattered small fields produce crude oil that will yield aviation gasoline, but the straight-run motor gasoline is of good quality and usually low in sulphur. Typical data on the aviation-gasoline yield are given for a few crude oils in Table IV. Desulphurization of naphtha from Healdton crude oil enables the attainment of 91-octane number gasoline. Oklahoma crude oils are not good sources of toluene or of C_7-naphthene, as indicated by the data in Table VI. Crude oils of the Oklahoma City type [40, 1938] are susceptible to superfractionation, and the combined iso-hexane-heptane-octane cuts, obtained by using such a high degree of fractionation that the hexanes, heptanes, and octanes of normal structure can be segregated from the corresponding iso-paraffins and cyclic compounds, yield 3·5% of aviation base stock that has a lean mixture aviation octane number with 4 ml. of tetraethyl lead of 94·5. The composition of these iso-cuts is given in Table XI, and a detailed report has been published by Ward *et al.* [41, 1947].

TABLE XI

Composition of Iso-cuts from Oklahoma City Crude Oil

Isohexane cut		*Isoheptane cut*		*Isooctane cut*	
		Paraffins			
	Vol. %		*Vol. %*		*Vol. %*
2,2-Dimethylbutane . .	3·9	*n*-Hexane .	1·4	*n*-Heptane .	3·3
2,3-Dimethylbutane . .	10·2	2,2-Dimethylpentane 2,4-Dimethylpentane	2·5	2,2-Dimethylhexane. .	5·3
2-Methylpentane .	47·0	2,3-Dimethylpentane 2-Methylhexane	21·5	2,5-Dimethylhexane 2,4-Dimethylhexane	1·1
3-Methylpentane	27·4	3-Methylhexane	16·1	2,3-Dimethylhexane. .	3·0
n-Hexane . .	1·6				
Total paraffins	90·1		41·5		12·7
		Naphthenes			
Cyclopentane .	9·8	Methylcyclopentane .	18·0	Methylcyclohexane. .	36·4
		Cyclohexane .	17·0	Ethylcyclopentane .	12·3
		1,1-Dimethylcyclopentane	1·4	Trimethylcyclopentanes .	17·3
		t-1,3-Dimethylcyclopentane	8·2		
		t-1,2-Dimethylcyclopentane	12·2		
Total naphthenes	9·8		56·8		66·0
		Aromatics			
Benzene . .	0·1	Benzene .	1·7	Toluene .	21·3
Total aromatics	0·1		1·7		21·3
Grand Total .	100·0		100·0		100·0

Detailed analyses of many Oklahoma crude oils are given in Bureau of Mines Reports of Investigations 3442 [6, 1939], 3592 [14, 1941], 3802 [7, 1945], and studies of the relationships of crude-oil characteristics and stratigraphy for parts of Oklahoma and Kansas have been reported by Neumann *et al.* [28, 1941].

Pennsylvania. Pennsylvania produced 0·71% of the Nation's 1945 crude oil and had estimated reserves of 0·5%. More than 85% of this State's 1945 production centred in the Bradford area. Pennsylvania paraffin-base crude oil is too well known to require extensive comment. The analysis in Table II. J is typical of the better grade. It yields excellent lubricating and Diesel fuels, but relatively poor gasoline in terms of octane number. Detailed analyses of crude oils in the Appalachian region are given in Bureau of Mines Report of Investigations 3385 [25, 1938].

Texas. The State of Texas produces almost as much crude oil as all the rest of the country. In 1945 its production was 43·77% of the U.S. total, and its estimated reserves were 55·7%. The fields listed in Table I represent 35·32% of the 1945 U.S. total and 48·8% of the reserves. Because Texas is so large in area and produces so many different types of crude oil, it is generally divided into districts or areas. That system has been used in reporting data in this article.

East Texas

This area includes the East Texas field, and the fields listed in Table I for this area yield 23% of Texas production. The crude oils are of two general types, Table II. H: those high in sulphur content, such as Cayuga (item 171), Hawkins (item 173), and Sulfur Bluff (item 177), and relatively low sulphur oils such as East Texas (item 172 [39]) and Long Lake (item 174). Crude oil produced from the Van (item 179 [39, 1945]) and Quitman fields are intermediate in sulphur content, although relatively high by comparison with other Mid-Continent intermediate-type oils. Most of these crude oils are too paraffinic to yield good aviation gasoline, as shown by the data in Table V, except by application of superfractionation. Neither are they particularly attractive for their toluene and C_7-naphthene content, as indicated in Table VI. Superfractionation of East Texas naphtha and virtual elimination of the normal paraffins will yield 7·2% of a composite of isohexane-heptane-octane cuts that will have a lean mixture aviation octane number of 91·3 with 4 ml. of tetraethyl lead. The composition of such a composite is indicated in Table XII.

TABLE XII

Composition of Iso-cuts from East Texas Crude Oil

Isohexane cut		*Isoheptane cut*		*Isooctane cut*	
		Paraffins			
	Vol. %		*Vol. %*		*Vol. %*
n-Pentane . .	5·6	*n*-Hexane .	2·6	*n*-Heptane .	1·1
2,2-Dimethylbutane . .	2·3	2,2-Dimethylpentane 2,4-Dimethylpentane	2·2	2,2-Dimethylhexane. .	1·5
2,3-Dimethylbutane . .	26·3	2,3-Dimethylpentane 2-Methylhexane	18·4	Methylpentanes . .	22·8
2-Methylpentane	29·8	3-Methylhexane	5·7	*n*-Octane .	0·8
3-Methylpentane	23·0				
n-Hexane . .	3·1				
Total paraffins	90·1		28·9		26·2
		Naphthenes			
Cyclopentane .	9·7	Methylcyclopentane .	19·3	Methylcyclohexane .	17·4
		Cyclohexane .	15·2	Ethylcyclopentane .	14·7
		1,1-Dimethylcyclopentane	5·2	Trimethylcyclopentanes .	11·0
		t-1,3-Dimethylcyclopentane	19·6	*t*-Dimethylcyclohexane	24·0
		t-1,2-Dimethylcyclopentane	11·7		
Total naphthas	9·7		71·0		67·1
		Aromatics			
Benzene . .	0·2	Benzene .	0·1	Toluene .	6·6
				Ethylbenzene	0·1
Total aromatics	0·2		0·1		6·7
Grand Total .	100·0		100·0		100·0

Upper Texas Gulf Coast

This area of Texas includes many fields that are excellent sources of aviation gasoline, and the fields listed in Table I produced approximately 20% of the crude oil in the State. The crude oils are, for the most part, classed as intermediate or naphthene in base, or a mixture of these two. In fact, most of the intermediate type miss the naphthene classification by a very narrow margin. Wax is present in some of the samples and absent in others, as indicated in Table II. H. The sulphur content and carbon residue are uniformly low. The data presented in Table V show the value of these crude oils as sources for aviation gasoline of 91-octane number. Certain of these crude oils, e.g. Conroe (item 185), are excellent sources for toluene, as they have a high content of both toluene and C_7-naphthenes for conversion to toluene, as the data in Table VI shows.

A number of analyses for the 97°–243° F. boiling-range naphtha are given in Table VII, where detailed data for products from Conroe, Hastings, Old Ocean, and Segno crude oils are presented. The wide range in paraffin, naphthene, and aromatic content is well illustrated by hydrocarbon-type analyses of naphthas from these same oils, as given in Table XIII.

TABLE XIII

Composition of Naphtha Fractions from Conroe, Hastings, Old Ocean, and Segno Crude Oils

	110°–200° F. Volume %			*200°–242° F. Volume %*		
	Paraffins	*Naphthenes*	*Aromatics*	*Paraffins*	*Naphthenes*	*Aromatics*
Conroe . .	44·0	48·7	7·3	19·9	50·7	29·4
Hastings . .	42·4	57·4	0·2	14·1	84·3	1·6
Old Ocean . .	59·5	36·2	4·3	33·3	54·0	12·7
Segno . . .	52·2	44·1	3·7	26·0	54·7	19·3
	242°–285° F. Volume %			*285°–320° F. Volume %*		
	Paraffins	*Naphthenes*	*Aromatics*	*Paraffins*	*Naphthenes*	*Aromatics*
Conroe . .	33·1	42·1	24·8	. .	. .	. .
Hastings* . .	18·4	76·6	5·0	. .	. .	. .
Old Ocean . .	47·9	37·2	14·9	55·0	28·8	16·2
Segno . . .	34·2	41·4	24·4	39·2	37·1	23·7

* Cut at 277° F.

Kraemer [18, 1938] has discussed some of the other refining characteristics of these crude oils.

Lower Texas Gulf Coast

The lower Gulf Coast region produced almost 9% of Texas crude oil in 1945. These oils, as Table II. H shows, are not essentially dissimilar from the upper Gulf Coast production. They yield excellent aviation gasoline, as the data in Table V indicate. However, while they are high in C_7-naphthenes, the toluene content of the fields given in Table VI does not approach that of some of the upper

TABLE XIV

Composition of Naphtha Fractions from Saxet, Tom O'Connor, and Plymouth Crude Oils

	Saxet Volume %			*Tom O'Connor Volume %*			*Plymouth Volume %*		
°F.	*Paraffins*	*Naphthenes*	*Aromatics*	*Paraffins*	*Naphthenes*	*Aromatics*	*Paraffins*	*Naphthenes*	*Aromatics*
100–200	32·2	67·8	0	51·9	47·1	1·0	47·4	51·6	1·0
200–242	12·1	87·9	0	22·4	69·7	7·9	18·7	76·8	4·5
242–285	13·3	81·3	5·4	33·9	53·6	12·5	26·6	65·7	7·7
285–320	12·1	85·1	2·8	33·9	55·1	11·0	23·8	69·0	7·2

Gulf Coast crude oils. Detailed hydrocarbon analyses of two fields in this area, Saxet (item 222) and Tom O'Connor (item 224), are given in Table VII. A comparison of naphthas from these two crude oils and one from the Plymouth field (item 219) on a hydrocarbon-type basis is given in Table XIV.

Kraemer [18, 1938] has discussed other refining characteristics of the crude oils from this area.

South and South Central Texas

This area produced 2·5% of the 1945 crude-oil production of Texas. For the most part they are naphthenic, wax-free oils that yield excellent aviation gasoline, as indicated by the data in Table V. The one sample tested for toluene, Rincon (item 234), has a high content of both toluene and C_7-naphthene (Table VI). A few of the oils, such as Darst Creek (item 229) and Luling (item 233), are intermediate-type oils with a relatively high sulphur content, about 0·9%. Both of these fields produce from the Edwards line. The crude oil produced in the Seven Sisters field (item 235), the Government Wells field (item 230), and Loma Novia field (item 232) contain no gasoline or kerosine. Kraemer [18, 1938] has discussed oils from this area.

North and West Central Texas

North and West Central Texas supplied 2·3% of Texas 1945 crude-oil production. The oils are of the intermediate type and wax-bearing, as shown in Table II. H. They do not yield good aviation gasoline, as indicated by the data in Table V, except by cutting to a low end-point or by superfractionation. Their toluene content is low, but the C_7-naphthene content is high, so they respond well to superfractionation and removal of the normal paraffins. Thus, Hull-Silk-Sikes (item 238) will yield 11·5% of mixed isohexane-heptane-octane cuts, having a lean mixture aviation octane number of 92·5 with 4 ml. tetraethyl lead. A detailed analysis of the iso-cuts from this crude oil is given in Table XV.

Table VII gives a detailed hydrocarbon analysis of the 97°–243° F. fraction from K.M.A. crude oil (item 239). As Table II. H shows, this oil is very similar in general characteristics to Hull-Silk-Sikes oil.

TABLE XV

Composition of Iso-cuts from Hull-Silk-Sikes Crude Oil

Isohexane cut	*Vol. %*	*Isoheptane cut*	*Vol. %*	*Isooctane cut*	*Vol. %*
		Paraffins			
n-Pentane	3·6	*n*-Hexane	1·2	*n*-Heptane	2·0
2,2-Dimethylbutane	0·8	2,2-Dimethylpentane 2,4-Dimethylpentane	1·7	2,2-Dimethylhexane	1·5
2,3-Dimethylbutane	12·1	2,3-Dimethylpentane 2-Methylhexane	17·1	Methylheptanes	10·1
2-Methylpentane	45·7	3-Methylhexane	13·8	*n*-Octane	0·5
3-Methylpentane	32·8			2,5-Dimethylhexane 2,4-Dimethylhexane	1·4
n-Hexane	2·6			2,3-Dimethylhexane	14·0
Total paraffins	97·6		33·8		29·5
		Naphthenes			
Cyclopentane	2·3	Methylcyclopentane	13·9	Methylcyclohexane	23·4
		Cyclohexane	9·5	Ethylcyclopentane	6·2
		1,1-Dimethylcyclopentane	2·4	Trimethylcyclopentanes	13·2
		t-1,3-Dimethylcyclopentane	15·8	*t*-Dimethylcyclohexane	22·1
		t-1,2-Dimethylcyclopentane	24·5		
Total naphthenes	2·3		66·1		64·9
		Aromatics			
Benzene	0·1	Benzene	0·1	Toluene	5·6
				Ethylbenzene	(trace)
Total aromatics	0·1		0·1		5·6
Grand Total	100·0		100·0		100·0

West Texas

This area of Texas has grown in importance as a producing district within the last few years. In 1945 it contributed almost 20% of the Texas output. The crude oils, as listed in Table II. H, are of two distinct types, the high-sulphur oil produced from the Permian limestone and the low-sulphur oil produced from the Ellenberger limestone. The Permian oils appear to be naphthenic; and some of them, such as Slaughter (item 263) and Wasson (item 266), contain unusually large quantities of aromatics. The sulphur compounds, as in the New Mexico oils, are largely aliphatic mercaptans and disulphides, and therefore can be

TABLE XVI

Composition of Naphtha Fraction from Slaughter, Wasson, and Yates Crude Oils

	Slaughter			*Wasson*			*Yates*		
°F.	*Paraffins*	*Naphthenes*	*Aromatics*	*Paraffins*	*Naphthenes*	*Aromatics*	*Paraffins*	*Naphthenes*	*Aromatics*
100–200	49·9	30·4	19·7	55·1	34·4	10·5	81·6	18·4	0
200–242	31·9	37·9	30·2	35·5	37·6	26·9	29·1	70·9	0
242–285	35·1	40·2	24·7	34·5	41·0	24·5	38·0	61·0	1·0
285–320	43·1	38·6	18·3	44·6	34·5	20·9	34·1	62·5	3·4

removed by modern treating methods. When this is done, a number of these oils will yield aviation-gasoline base stock, although generally an end-point of about 225° F. is necessary. Data showing the effect of desulphurization over bauxite [17, 1943] is given in Table IV. The toluene and C_7-naphthene data in Table VI show considerable difference from field to field. Comparative data on the composition of the naphtha for Slaughter and Wasson crude oils are given in Table XVI, together with similar data for naphtha from Yates.

The crude oil from the Yates field (item 267) deserves specific mention because it, together with a few Winkler county oils, is unique in having a very high content of iso-paraffins in the aviation-gasoline range and almost no normal paraffins. As a result, the response of these naphthas to desulphurization is exceptionally good. These oils also are almost devoid of aromatics.

A typical analysis of the sulphur compounds [5, 1941; 17, 1943] for Slaughter 390° F. end-point naphtha is given in Table XVII.

TABLE XVII

Group Sulphur Analysis of Slaughter Naphtha

	Weight %	
	Untreated naphtha	*Desulphurized naphtha*
Hydrogen sulphide	0·000	0·000
Free sulphur . .	0·000	0·000
Mercaptans . .	0·181	0·000
Disuphides . . .	0·000	0·000
Aliphatic sulphides	0·028	0·000
Aromatic sulphides	0·052	0·006
Residual sulphur .	0·004	0·005
Total sulphur .	0·265	0·011

Desulphurization of these West Texas naphthas is discussed further by Guthrie and Simmons [17, 1943], and detailed analyses of West Texas crude oils are given by Guthrie [16, 1944].

Panhandle Texas

The Texas Panhandle produces paraffin-intermediate wax-bearing crude oil containing appreciable quantities of hydrogen sulphide. This area produced about 1·8% of the total 1945 production in Texas. Typical analyses are given by Tydeman and Kellogg [40, 1938]. The oils are not suitable sources for aviation gasoline; but, except for the sulphur contents, are better than many Mid-Continent crude oils for general refinery purposes. Beside the reference to West Texas crude oil above, detailed analyses of Texas oils are given by Kraemer and Wade [20, 1939] and by Lane [22, 1943].

Wyoming

In 1945 Wyoming produced 2·12% of the Nation's total output and had 2·9% of its reserves. The fields listed in Table I represent 1·48% of the U.S. 1945 production and 2·28% of the reserves. Wyoming crude oils usually are divided into two classes, as shown in Table II. I. These are the low-sulphur oils typified by the production in Lance Creek (item 275), Lost Soldier (item 276), and Salt Creek (item 278), and the high-sulphur 'black oils', such as Byron (item 271), Frannie (item 273), and Oregon Basin (item 277) crude oils. The low-sulphur oils are of intermediate or paraffin types and wax-bearing and conform in most respects to the characteristics expected of this type of oil. These oils do not yield distillates suitable for aviation gasoline, as indicated in Table IV, and they are not good sources for toluene and C_7-naphthenes, as shown by the data in Table VI.

Potential reserves of the 'black oils' of Wyoming are believed to be much greater than those normally estimated. These oils are difficult to refine because of the high sulphur content and the fact that many of the sulphur compounds present have cyclic structures that make the compounds difficult to remove by conventional refining methods. It is beyond the scope of this report to discuss the refining of these oils; Thorne and Murphy [36, 1932] and Ball [5, 1941] have discussed the subject in detail. As a corollary to their high sulphur content, these crude oils also have high contents of good-quality asphalts, which have been the subject of extensive studies by Stanfield [34, 1934; 35, 1941]. Crawford and Larson [10, 1943] have studied the relationships of crude-oil characteristics and stratigraphy in the Rocky Mountain region and have presented an interesting discussion. Detailed analyses of Wyoming crude oils are given by Thorne and Murphy [36, 1932; 37, 1937].

The crude oil produced in the Elk Basin field (which extends into Montana), although high in sulphur content, apparently does not contain the cyclic sulphur compounds that are present in the 'black oils', as naphtha from this oil can be desulphurized successfully by catalytic treatment with bauxite. For example, a naphtha cut between 110° and 285° F., representing 15·1% of the crude oil, has a lean mixture aviation octane number of 71·3 undesulphurized and 80·4 desulphurized, using 4 ml. tetraethyl lead. Table XVIII gives the group sulphur analysis of this naphtha before and after desulphurization.

TABLE XVIII

Group Sulphur Analysis of Elk Basin Naphtha

	Weight %	
	Undesulphurized	*Desulphurized*
Hydrogen sulphide	0·003	0·000
Mercaptans . .	0·050	0·000
Free sulphur . .	0·000	0·000
Disulphides . .	0·003	0·000
Aliphatic sulphides	0·010	0·000
Aromatic sulphides	0·000	0·000
Residual sulphur .	0·001	0·002
Total sulphur .	0·067	0·002

The composition of naphtha fractions from this crude oil is given in Table XIX.

TABLE XIX

Composition of Naphtha Fraction from Elk Basin Crude Oil

Boiling-range, cut point, °F.	*Volume %*		
	Paraffins	*Naphthenes*	*Aromatics*
110–200	27·2	21·2	1·6
200–242	52·2	34·7	13·1
242–285	50·8	33·4	15·8
285–320	53·8	30·2	16·0

Future Trends

One fact of interest can be noted from a general comparison of the crude oils produced 10 or more years ago with those produced to-day from newly discovered deep horizons. The new oils usually are more paraffinic and contain larger amounts of the more volatile fractions. In a ber of fields this trend has gone so far that 90 to 100% he material boils below 600° F. In such fields the rocarbon mixture is usually present in the producing horizon as a vapour under high pressure, and the liquids are formed by a phenomenon known as retrograde condensation when the pressure is reduced. Hydrocarbons produced in this manner are known as 'condensates' and are becoming of increasing importance in the production picture. Most of them are highly paraffinic, but a few are naphthenic.

In the introduction the changes in fuels to meet new or improved engines were mentioned. These are reflected in present-day demands for very high octane number aviation fuel for reciprocating-type engines, fuels for gas-turbo type engines, large volumes and improved quality of Diesel fuels, and improved lubricating oils. To meet some of these demands, catalytic cracking processes have been introduced and highly developed, as well as solvent-treating methods of several types.

All these requirements and developments have intensified the need for more detailed information on the compositions and properties of crude oil and its products. The data in this article in Tables VIII to XIX present information that relates directly to this new trend in crude-oil analysis, particularly as applied to aviation gasoline. The next few years will see great development in analytical methods and information on composition for the 300°–700° F. boiling-range material, and possibly for the lubricating oils also.

REFERENCES

1. *Amer. Inst. Min. Met. Eng., Trans., Pet. Dev. and Tech.* 160, 258 et seq. (1945).
2. Amer. Soc. Test Materials, 1944 Standards, Part III, Designation D614–44T, p. 1242 (1944).
3. —— Designation D86–40, p. 136 (1944).
4. —— Designation D323–43, p. 260 (1944).
5. Ball, J. S. Bur. Mines Rept. Investigations 3591 (1941).
6. Blade, O. C. Bur. Mines Rept. Investigations 3442 (1939).
7. —— Bur. Mines Rept. Investigations 3802 (1945).
8. Blade, O. C., and Branner, G. C. Bur. Mines Rept. Investigations 3486 (1940).
9. Blade, O. C., and Garton, E. L. Bur. Mines Rept. Investigations 4034 (1947).
10. Crawford, J. G., and Larson, R. M. *Amer. Asso. Pet. Geol., Bull.* **27**, 1305 (1943).
11. Dean, E. W., *et al.* Bur. Mines Bull. 207 (1922).
12. Garton, E. L. Bur. Mines Rept. Investigations 3346 (1937).
13. —— Bur. Mines Rept. Investigations 3476 (1939).
14. —— Bur. Mines Rept. Investigations 3592 (1941).
15. Gooding, R. M., Adams, N. G., and Rall, H. T. *Ind. Eng. Chem., Anal. Ed.* **18**, 2 (1946).
16. Guthrie, B. Bur. Mines Rept. Investigations 3744 (1944).
17. Guthrie, B., and Simmons, M. C. Bur. Mines Rept. Investigations 3729 (1943).
18. Kraemer, A. J. *Science of Petroleum*, vol. ii, p. 858 (1938).
19. Kraemer, A. J., and Lane, E. C. Bur. Mines Bull. 401 (1937).
20. Kraemer, A. J., and Wade, G. Bur. Mines Tech. Paper 607 (1939).
21. Lane, E. C. Bur. Mines Rept. Investigations 3660 (1942).
22. —— Bur. Mines Rept. Investigations 3699 (1943).
23. Lane, E. C., and Garton, E. L. Bur. Mines Rept. Investigations 3279 (1935).
24. —— Bur. Mines Rept. Investigations 3362 (1937).
25. —— Bur. Mines Rept. Investigations 3385 (1938).
26. —— Bur. Mines Rept. Investigations 3688 (1943).
27. Merrill, D. R. *Science of Petroleum*, vol. ii, p. 851 (1938).
28. Neumann, L. M., *et al. Bull. Amer. Asso. Pet. Geol.* **25**, 1801 (1941).
29. *Oil and Gas J.*, Annual Number, 44, 26 Jan. 1946.
30. Rees, D. W., Henline, P. W., and Bell, A. H. Ill. State Geol. Surv. Rept. Investigations 88 (1945).
31. Smith, N. A. C., and Lane, E. C. Bur. Mines Bull. 291 (1928).
32. Smith, H. M. Bur. Mines Rept. Investigations 3532 (1940).
33. —— Bur. Mines Tech. Paper 610 (1940).
34. Stanfield, K. E. Bur. Mines Rept. Investigations 3435 (1934).
35. —— Bur. Mines Rept. Investigations 3568 (1941).
36. Thorne, H. M., and Murphy, W. Bur. Mines Tech. Paper 538 (1932).
37. —— Bur. Mines Rept. Investigations 3358 (1937).
38. —— Bur. Mines Rept. Investigations 3423 (1938).
39. Thorne, H. M., Murphy, W., and Ball, J. S. *Ind. Eng. Chem., Anal. Ed.* **17**, 481 (1945).
40. Tydeman, F. W. L., and Kellogg, C. M. *Science of Petroleum*, vol. ii, p. 840 (1938).
41. Ward, C. C., Gooding, R. M., and Eccleston, B. H. *Ind. Eng. Chem.* **39**, 105 (1947).

THE CRUDE OILS OF VENEZUELA

Data from Gulf Refining Co., Pittsburgh, U.S.A.

VENEZUELA CRUDES

				Crude properties								*0–392° F. Gasoline*			*392–428° F. Naphtha*		*428–518° F. Gas oil*		*Bottoms or residue*						
						Saybolt Univ. Visc.															*S.U. Visc.*				
Field	*Sample date*	*Producing zone*	*Depth ft.*	*Colour*	*Grav. A.P.I.*	*85° F.*	*100° F.*	*122° F.*	*210° F.*	*% Sul.*	*Pour °F.*	*Vol. %*	*Grav. A.P.I.*	*O.N. A.S.T.M.*	*Vol. %*	*Grav. A.P.I.*	*Vol. %*	*Grav. A.P.I.*	*Vol. %*	*Grav. A.P.I.*	*130° F.*	*210° F.*	*Pour °F.*	*% Sul.*	*C.R. %*
Bachaquero	12/4/44	La Rosa	4,069–199	Dk. brown	17·5	1,178	628	380	81	2·56	−25	11·8	52·0	64·0	2·6	36·9	7·4	32·8	77·3	11·8	365	..	40	2·91	12·04
Taparito	23/12/41	La Rosa	Approx. 1,800–3,200	„	14·8	..	4,137	1,717	697	2·43	−10	2·9	47·6	..	1·4	37·2	5·6	32·7	89·8	12·8	4,098	342	10	2·43	10·7
Cabimas	23/12/41	La Rosa	Approx. 1,500–3,000	„	22·1	442	286	182	..	2·01	B−50	14·0	55·3	..	2·6	40·1	6·8	35·7	75·9	15·8	1,302	171	+15	2·33	8·51
Lagunillas	23/12/41	La Rosa	Approx. 3,000–5,000	„	17·8	1,827	992	503	..	2·14	−20	9·5	52·8	..	2·2	38·1	6·5	33·7	81·5	13·4	3,469	316	+35	2·54	10·8
Jusepin	31/8/44	La Pica	Approx. 3,500–5,200	Gr. brown	31·2	68·3	56·1	48·7	..	1·08	+50	24·3	55·9	55·0	3·5	42·1	10·5	37·1	61·3	21·8	263	631	+80	1·53	4·29
Mulata	24/8/44	La Pica	Approx. 4,300–6,000	„	34·0	49·8	45·6	41·8	..	0·80	+50	27·4	56·5	57·0	3·6	42·1	10·7	37·3	57·7	23·4	160	53	+80	1·28	2·88
Santa Rosa	2/11/45	Merecure	10,296–324	Dk. green	34·4	Waxy	Waxy	43·8	34·0	0·29	+95	15·4	51·0	59·0	3·5	40·8	9·2	35·4	69·8	30·4	63	41	+115	0·36	1·41
Calentura	15/2/46	Cretaceous	10,146–290	„	10·5	8,323	4,431	1,981	24·1	5·29	+5	10·3	55·0	48·0	2·7	41·3	8·6	33·4	77·1	2·2	3,398	390	45	6·26	25·2
Guara	28/2/46	F4 Sand	5,709–27	Dk. brown	37·8	41·7	38·8	36·0	..	0·54	+50	37·0	58·0	52·0	5·0	43·7	13·3	38·3	43·8	22·9	189	58	95	1·04	4·29
„	10/2/46	T Sand	6,516–30	„	17·2	3,886	2,138	941	143	1·95	0	10·1	54·7	56·0	2·4	39·7	6·7	34·8	79·9	11·8	..	708	+65	2·45	15·74
Calco Seco	14/1/46	JL Sand	5,668–73	Bl. brown	49·0	31·4	30·6	30	..	0·10	+5	51·2	57·1	48·0	8·1	46·8	21·0	42·5	18·6	35·0	44·8	34·6	+80	0·22	0·72
Santa Ana	9/9/46	Verde B	4,652–70	Dk. brown	40·5	..	..	35·4	..	0·24	+95	37·1	58·7	56·0	2·7	43·9	11·3	37·7	48·1	30·2	..	42	+120	0·45	1·41
Pueblo Viejo	19/9/46	Eocene	1,810–25	„	18·9	535	339	201	55·2	1·57	−30	11·4	50·5	68·0	3·0	37·4	8·0	32·1	76·8	13·6	1,246	147	+10	1·98	8·61
„	21/9/46	Eocene	2,270–310	„	24·8	99	78	61	38	0·98	B−50	17·2	48·1	66·0	5·0	38·1	10·6	32·5	66·7	18·1	282	66	−25	1·29	4·75

THE CRUDE OILS OF SAUDI ARABIA

Contribution from the Arabian-American Oil Company

The first discovery of oil in Saudi Arabia was in 1935 in the Dammam field which is located in the south-eastern part of Hasa about 6 miles from the Persian Gulf coastline and due west of the north end of Bahrein Island. Production is from the Arab Zone in Dolomitic and Oolitic Limestone formation at a depth of 4,700 ft. Present daily production rate is about 25,000 bbl. The crude is a 35-gravity paraffin-intermediate-base oil. Light distillate products are decidedly paraffinic, giving relatively low octane-number gasolines, light-gravity and good burning-quality kerosines, and high cetane-number gas oils.

A second field, discovered in 1940, is Abu Hadriya in the north-eastern part of Hasa, approximately 120 miles north-west of the Dammam field. Production was found in the Dolomitic and Oolitic Limestone of the Hadriya Zone at a depth of 10,200 ft. The discovery well was shut in and there is no current production from the field. Crude from this well was very similar to Dammam although somewhat more paraffinic.

Potentially the greatest field so far discovered is Abqaiq, located in the southern part of Hasa, approximately 40 miles south-west of Dammam field, and was first brought in during 1941. However, all wells were shut in and the field was only reopened in 1945. Present daily production is approximately 380,000 bbl. and development is now going ahead quite rapidly. Two pay zones, known as 'C' member Arab Zone and 'D' member Arab Zone, were discovered, but only the latter zone is being produced currently. Both are in Dolomitic and Oolitic Limestone formation. The 'D' member crude, which is produced from depths ranging from 5,900 to 7,200 ft., is about 37 gravity and, except for a greater proportion of low boiling-fractions, is very similar to Dammam. The 'C' member crude was found at depths between 5,800 and 6,500 ft. Samples tested have ranged from 19 to 35 gravity, but generally were much lower in gravity and considerably more asphaltic than 'D' member crude. Tests on intermediate-gravity sample are shown in Table I.

The newest field in Arabia is Qatif, located in the east central part of Hasa, approximately 20 miles north of Dammam field, but there is a more recent field at Am Dar. Six wells have been drilled and were brought in since 1945, discovering oil in both the 'C' member Arab Zone at 7,080 ft. and 'D' member Arab Zone at 7,250 ft. Current production is at the rate of about 10,000 bbl. daily. The 'D' member oil is quite similar to Abqaiq, but the 'C' member oil is more asphaltic and resembles Bahrein crude.

Crude oil tests, also typical yields and characteristics of products from distillation of each of the currently available Arabian crude oils, are shown in Table I. Arbitrary cut-points have been selected, but those chosen will serve to illustrate yield and quality obtainable. It will be observed that Arabian crudes are relatively high in sulphur content. This sulphur is concentrated in the heavier fractions and is predominantly in the form of thiophenes, which are stable thermally, relatively inactive, and non-corrosive. Consequently there is little formation of hydrogen sulphide in the crude distillation of Arabian crudes. All off-shore shipments of Arabian crudes are stabilized in the field where substantially all propane and lighter hydrocarbons are removed, thus producing hydrogen sulphide-free crude. Therefore, crude distillation-unit furnaces, transfer lines, fractionating columns, &c., do not require special alloy materials for corrosion protection but may be of carbon steel. In reforming and cracking, the sulphur also concentrates in the heavier fractions, but some breakdown of the sulphur compounds does occur and the usual chrome alloy furnace tubes, headers, transfer lines, tower linings, &c., are required.

Arabian crude oils offer considerable flexibility to the refiner in manufacturing petroleum products to meet his particular needs. This will be evident from the discussion of some of the more pertinent refining characteristics which follow.

Gasoline

Straight-run gasoline yields up to approximately 30% may be obtained from Arabian crudes. The total gasoline cut is relatively low in octane number, but good octanes are readily obtained with appropriate refining facilities. A suggested method of processing is to cut a light straight-run gasoline to 200° F. end-point and about 62·5 octane number, and thermally reform the heavy fraction. Thermal reforming of this fraction gives octane numbers of 68–72 on debutanized reformed gasoline and up to 75-octane number on essentially full-butane retention-reformed gasoline.

Distillate and residual fractions not needed for kerosine, Diesel, lubricating oils, or other special products may be cracked. Residuum after 40-viscosity gas oil when thermally cracked yields up to 40% of 66–8-octane number gasoline. An overall yield of 35 to 40% of gasoline of approximately 67-clear-octane number is thus obtained from the combined crude stilling, reforming, and cracking operations. The gasoline yield may be increased to 60–5% by cracking the kerosine distillate and gas-oil cuts as well.

Kerosine

Kerosine distillate yields in excess of 20% may be obtained from Arabian crude. Although these raw distillates have an aromatic content of approximately 20%, they exhibit relatively high burning quality. It is thus possible to make a fair quality kerosine by selecting a cut having maximum sulphur of 0·10% and sweetening only. Yields of 15% kerosine below 0·10% sulphur content are possible with some sacrifice of gasoline; from 4 to 5% yield may be obtained when cutting a 390° F. end-point straight-run gasoline. Realization of maximum kerosine of excellent burning quality is possible with sulphur dioxide refining using moderate dosages. Good-quality kerosine also may be made by acid treating and re-running, but I.P. smoke-points will be somewhat lower than the 45 mm. readily attainable by sulphur dioxide refining.

Diesel Oils

Arabian crude is an excellent source of high-quality Diesel fuel of both automotive and industrial grades. Yields of 30 to 35% are not unusual. Automotive Diesel oils have exceptionally high cetane numbers of 58–60 and slightly lower for the industrial grades. Because of the

TABLE I

Crude Oils of Saudi Arabia

Crude	*Dammam*	*Abqaiq*		*Qatif*		*Abu Hadriya*
Location	South-eastern part of Hasa, approximately 6 miles from Persian Gulf coastline, due west of north end of Bahrein Island	Southern part of Hasa, approximately 40 miles south-west of Dammam field		East central part of Hasa, approximately 20 miles north of Dammam field		North-eastern part of Hasa, approximately 120 miles north-west of Dammam field
Discovery date of pool	1935	1941		1945		1940
Approximate						
Producing depths (ft.)	4,700	6,500		7,200		10,200
Producing formations	Dolomitic and Oolitic Limestone, Arab Zone	Dolomitic and Oolitic Limestone		Dolomitic and Oolitic Limestone		Dolomitic and Oolitic Limestone, Hadriya Zone
		'C' Member Arab Zone	*'D' Member Arab Zone*	*'C' Member Arab Zone*	*'D' Member Arab Zone*	
Gravity, °A.P.I.	35	27	37	30	36	35
Viscosity, S.S.U. at 100° F.	41	89·5	40·2	65·6	42·9	48·6
Pour-point, °F.	−15	0	−15	0	−5	..
Sulphur, wt. %	1·4–1·6	2·3	1·3–1·5	2·5	1·5	1·56
Paraffin wax, Holde, %	2·0–3·8	1·0	1·7–3·1	3·1	2·5	3·6
Yields by volume:						
Gasoline						
340° F. end-point	23·0	..	26·3	19·0	26·0	..
390° F. end-point	30·8	..	34·5	25·0	33·0	..
Kerosine						
After 340° F. end-point gasoline	23·2	..	20·5	19·0	21·0	..
After 390° F. end-point gasoline	10·8	..	8·7	9·0	9·0	..
Gas oil						
After 390° F. end-point gasoline	42·0	..	38·0	38·0	40·0	..
Residuum						
After 390° F. end-point gasoline	69·2	..	65·5	75·0	67·0	..
After 400 viscosity kerosine	58·4	..	56·8	66·0	58·0	..
After 40 viscosity gas oil	27·2	..	27·5	37·0	27·0	..
Tests:						
Gasoline—340° F. end-point						
Gravity, °A.P.I.	61·7	..	66·3	66·6	65·0	..
Initial boiling-point, °F.	105	..	85	106	106	..
Final boiling-point, °F.	340	..	340	340	340	..
Distilling up to 212° F. (100° C.)	31%	..	36%	36%	33%	..
Sulphur, wt. %	0·032	..	0·037	0·043	0·061	..
Gasoline—390° F. end-point						
Gravity, °A.P.I.	58·2	..	61·6	62·3	61·2	..
Initial boiling-point, °F.	111	..	91	116	114	..
Final boiling-point, °F.	390	..	390	390	390	..
Distillation up to 212° F. (100° C.)	20%	..	25%	23%	25%	..
Sulphur, wt. %	0·035	..	0·040	0·059	0·078	..
Kerosine—After 340° F. end-point gasoline						
Gravity, °A.P.I.	43·9	..	45·5	44·7	44·7	..
Initial boiling-point, °F.	370	..	363	370	372	..
Final boiling-point, °F.	514	..	560	514	531	..
Viscosity, Saybolt thermo. at 60° F.	360	..	360	360	360	..
Sulphur, wt. %	0·18	..	0·20	0·27	0·20	..
Kerosine—After 390° F. end-point gasoline						
Gravity, °A.P.I.	43·6	..	44·4	44·6	44·4	..
Initial boiling-point, °F.	406	..	414	408	410	..
Final boiling-point, °F.	486	..	475	476	510	..
Viscosity, Saybolt thermo. at 60° F.	400	..	400	400	400	..
Sulphur, wt. %	0·15	..	0·20	..	0·17	..
Gas oil—After 390° F. end-point gasoline						
Gravity, °A.P.I.	35·0	..	35·1	34·2	35·5	..
Initial boiling-point, °F.	426	..	430	430	440	..
Final boiling-point, °F.	742	..	722	739	749	..
Distilling up to 572° F. (300° C.)	52%	..	53%	58%	50%	..
Viscosity, S.S.U. at 100° F.	40	..	40	40	40	..
Sulphur, wt. %	1·13	..	1·10	1·83	1·26	..
Residuum—After 390° F. end-point gasoline						
Gravity, °A.P.I.	26·5	..	26·7	22·2	27·1	..
Viscosity, S.S.U. at 130° F.	62	..	66	103	62	..
Viscosity, S.S.U. at 210° F.	39	..	40	47	39	..
Sulphur, wt. %	2·0	..	1·9	3·0	2·2	..
Residuum—After 400 viscosity kerosine						
Gravity, °A.P.I.	23·8	..	24·2	18·8	24·3	..
Viscosity, S.S.U. at 130° F.	97	..	96	196	68	..
Viscosity, S.S.U. at 210° F.	46	..	46	60	44	..
Sulphur, wt. %	2·2	..	2·1	3·6	2·4	..
Residuum—After 40 viscosity gas oil						
Gravity, °A.P.I.	15·3	..	16·0	11·2	16·4	..
Viscosity, S.S.U. at 130° F.	1,450	..	1,369	3,566	1,082	..
Viscosity, S.S.U. at 210° F.	179	..	175	338	155	..
Sulphur, wt. %	3·1	..	2·8	4·1	3·2	..

relatively high wax content of the heavier fractions, their use may be limited where low pour-points are required. However, high yields of low-pour Diesel are possible by inclusion of the fractions normally produced as kerosine. For example, the 30% cut of Dammam crude beginning at 30% and ending at 60% of crude has a zero pour and 59 cetane number. The gas-oil cuts from Arabian crudes are also good sources of both thermal and catalytic cracking stocks.

Lubricating Oils

Both distillate and residual oils from Arabian crude may be processed to produce high-quality lubricating oils. A combination of deasphalting, solvent refining, and dewaxing may be effectively employed for the production of excellent quality, high viscosity-index lubricating oils. Illustrative of the yields and quality of oils which may be manufactured are the three processing diagrams shown in Tables II to IV inclusive. These diagrams, prepared by Texaco Development Corporation and presented with their permission, are based on using propane deasphalting, furfural refining, and ketone-benzol dewaxing. However, other solvent refining processes, such as duo-sol, would give similar results. 60 to 80-viscosity-index oils may be made by light acid treatment and dewaxing of distillate cuts for total yields from crude of approximately 15%.

The sulphur content of lubricating oils from Arabian crude is relatively high. Extensive laboratory tests conducted on motor, Diesel, aircraft, and gear oils have indicated that the high sulphur content of oils produced from Arabian crude may be greatly beneficial with respect to corrosion, oxidation, and engine cleanliness.

Wax

The wax content of Arabian crude is concentrated in the 50 to 80% fraction from crude, the highest concentration being the middle half of this fraction. Cracking of this particular fraction improves the pour-point of the residual fuel. Also, this waxy gas oil may be processed by conventional methods to produce fair yields of good-quality wax for commercial sale. Melting-points of this wax range upward to approximately 135° F.

Asphalts

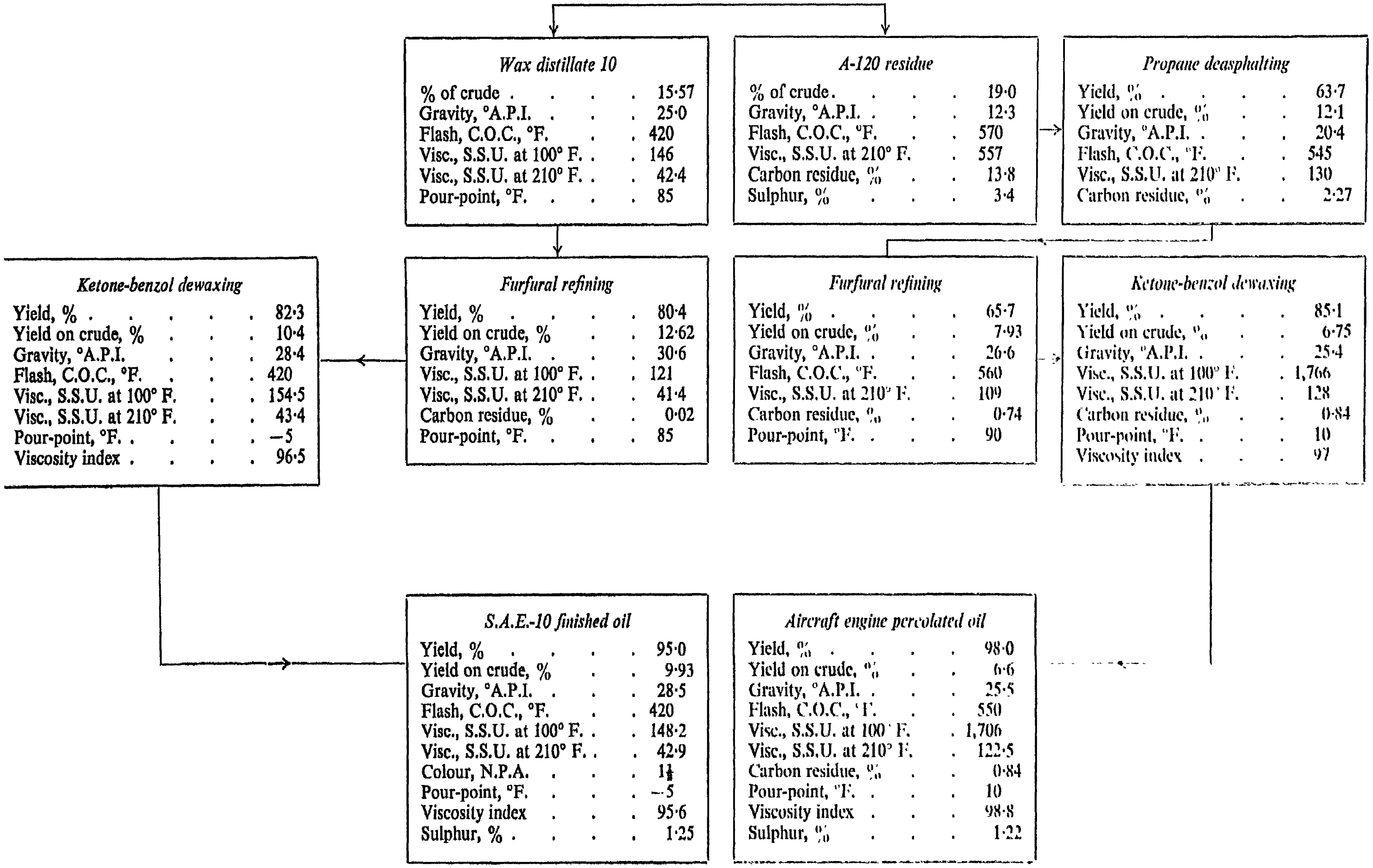
Residua from Arabian crudes show promise for production of both steam-refined and air-blown asphalts, although the yields from the lighter 35–7 gravity crudes naturally are low. However, Arabian crudes about to be produced will yield 7 to 8% of good asphalt by vacuum reduction of the residua to 7°–8° A.P.I. with air blowing to the desired penetration.

TABLE II

Processing Arabian Crude for Lubricating Oil Products

OPERATION 'A'

VACUUM DISTILLATION UNIT CHARGING TOPPED CRUDE



Wax distillate 10	
% of crude	15·57
Gravity, °A.P.I.	25·0
Flash, C.O.C., °F.	420
Visc., S.S.U. at 100° F.	146
Visc., S.S.U. at 210° F.	42·4
Pour-point, °F.	85

A-120 residue	
% of crude	19·0
Gravity, °A.P.I.	12·3
Flash, C.O.C., °F.	570
Visc., S.S.U. at 210° F.	557
Carbon residue, %	13·8
Sulphur, %	3·4

Propane deasphalting	
Yield, %	63·7
Yield on crude, %	12·1
Gravity, °A.P.I.	20·4
Flash, C.O.C., °F.	545
Visc., S.S.U. at 210° F.	130
Carbon residue, %	2·27

Ketone-benzol dewaxing	
Yield, %	82·3
Yield on crude, %	10·4
Gravity, °A.P.I.	28·4
Flash, C.O.C., °F.	420
Visc., S.S.U. at 100° F.	154·5
Visc., S.S.U. at 210° F.	43·4
Pour-point, °F.	−5
Viscosity index	96·5

Furfural refining	
Yield, %	80·4
Yield on crude, %	12·62
Gravity, °A.P.I.	30·6
Visc., S.S.U. at 100° F.	121
Visc., S.S.U. at 210° F.	41·4
Carbon residue, %	0·02
Pour-point, °F.	85

Furfural refining	
Yield, %	65·7
Yield on crude, %	7·93
Gravity, °A.P.I.	26·6
Flash, C.O.C., °F.	560
Visc., S.S.U. at 210° F.	109
Carbon residue, %	0·74
Pour-point, °F.	90

Ketone-benzol dewaxing	
Yield, %	85·1
Yield on crude, %	6·75
Gravity, °A.P.I.	25·4
Visc., S.S.U. at 100° F.	1,766
Visc., S.S.U. at 210° F.	128
Carbon residue, %	0·84
Pour-point, °F.	10
Viscosity index	97

S.A.E.-10 finished oil	
Yield, %	95·0
Yield on crude, %	9·93
Gravity, °A.P.I.	28·5
Flash, C.O.C., °F.	420
Visc., S.S.U. at 100° F.	148·2
Visc., S.S.U. at 210° F.	42·9
Colour, N.P.A.	1¼
Pour-point, °F.	−5
Viscosity index	95·6
Sulphur, %	1·25

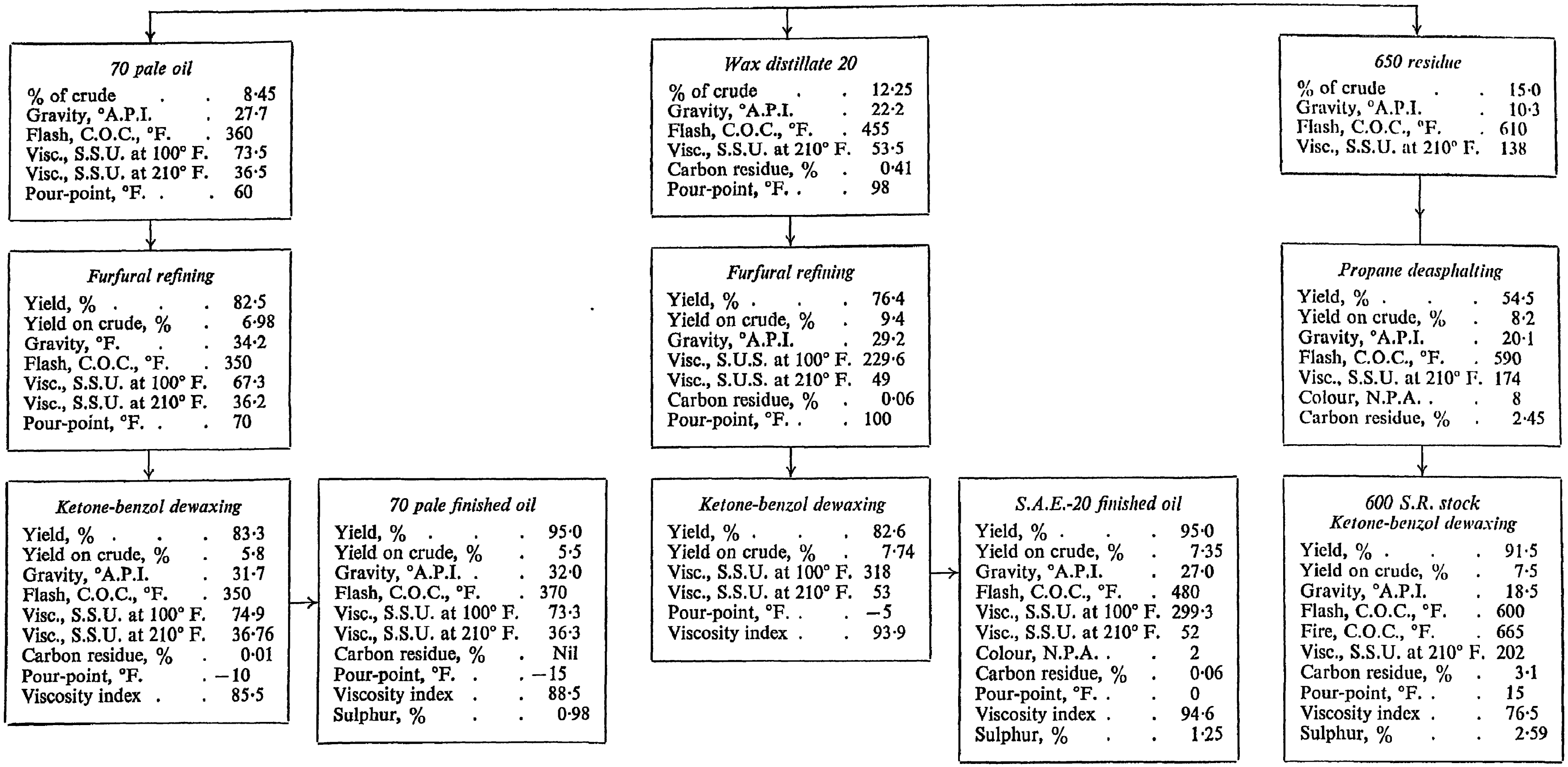
Aircraft engine percolated oil	
Yield, %	98·0
Yield on crude, %	6·6
Gravity, °A.P.I.	25·5
Flash, C.O.C., °F.	550
Visc., S.S.U. at 100° F.	1,706
Visc., S.S.U. at 210° F.	122·5
Carbon residue, %	0·84
Pour-point, °F.	10
Viscosity index	98·8
Sulphur, %	1·22

TABLE III

Processing Arabian Crude for Lubricating Oil Products

OPERATION 'B'

VACUUM DISTILLATION UNIT CHARGING TOPPED CRUDE



70 pale oil	
% of crude	8·45
Gravity, °A.P.I.	27·7
Flash, C.O.C., °F.	360
Visc., S.S.U. at 100° F.	73·5
Visc., S.S.U. at 210° F.	36·5
Pour-point, °F.	60

Furfural refining	
Yield, %	82·5
Yield on crude, %	6·98
Gravity, °F.	34·2
Flash, C.O.C., °F.	350
Visc., S.S.U. at 100° F.	67·3
Visc., S.S.U. at 210° F.	36·2
Pour-point, °F.	70

Ketone-benzol dewaxing	
Yield, %	83·3
Yield on crude, %	5·8
Gravity, °A.P.I.	31·7
Flash, C.O.C., °F.	350
Visc., S.S.U. at 100° F.	74·9
Visc., S.S.U. at 210° F.	36·76
Carbon residue, %	0·01
Pour-point, °F.	−10
Viscosity index	85·5

70 pale finished oil	
Yield, %	95·0
Yield on crude, %	5·5
Gravity, °A.P.I.	32·0
Flash, C.O.C., °F.	370
Visc., S.S.U. at 100° F.	73·3
Visc., S.S.U. at 210° F.	36·3
Carbon residue, %	Nil
Pour-point, °F.	−15
Viscosity index	88·5
Sulphur, %	0·98

Wax distillate 20	
% of crude	12·25
Gravity, °A.P.I.	22·2
Flash, C.O.C., °F.	455
Visc., S.S.U. at 210° F.	53·5
Carbon residue, %	0·41
Pour-point, °F.	98

Furfural refining	
Yield, %	76·4
Yield on crude, %	9·4
Gravity, °A.P.I.	29·2
Visc., S.U.S. at 100° F.	229·6
Visc., S.U.S. at 210° F.	49
Carbon residue, %	0·06
Pour-point, °F.	100

Ketone-benzol dewaxing	
Yield, %	82·6
Yield on crude, %	7·74
Visc., S.S.U. at 100° F.	318
Visc., S.S.U. at 210° F.	53
Pour-point, °F.	−5
Viscosity index	93·9

S.A.E.-20 finished oil	
Yield, %	95·0
Yield on crude, %	7·35
Gravity, °A.P.I.	27·0
Flash, C.O.C., °F.	480
Visc., S.S.U. at 100° F.	299·3
Visc., S.S.U. at 210° F.	52
Colour, N.P.A.	2
Carbon residue, %	0·06
Pour-point, °F.	0
Viscosity index	94·6
Sulphur, %	1·25

650 residue	
% of crude	15·0
Gravity, °A.P.I.	10·3
Flash, C.O.C., °F.	610
Visc., S.S.U. at 210° F.	138

Propane deasphalting	
Yield, %	54·5
Yield on crude, %	8·2
Gravity, °A.P.I.	20·1
Flash, C.O.C., °F.	590
Visc., S.S.U. at 210° F.	174
Colour, N.P.A.	8
Carbon residue, %	2·45

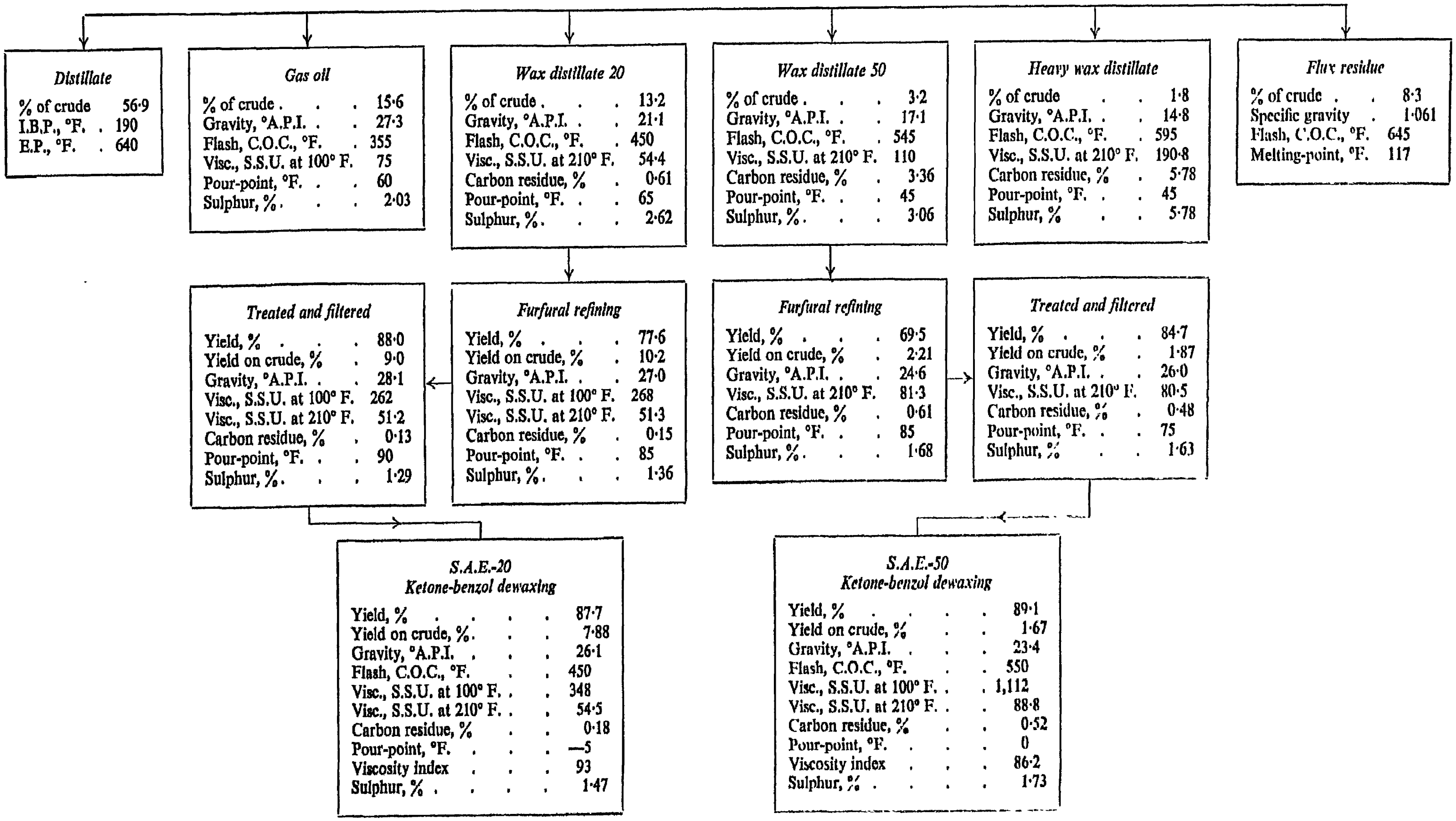
600 S.R. stock *Ketone-benzol dewaxing*	
Yield, %	91·5
Yield on crude, %	7·5
Gravity, °A.P.I.	18·5
Flash, C.O.C., °F.	600
Fire, C.O.C., °F.	665
Visc., S.S.U. at 210° F.	202
Carbon residue, %	3·1
Pour-point, °F.	15
Viscosity index	76·5
Sulphur, %	2·59

TABLE IV

Processing Arabian Crude for Lubricating Oil Products

OPERATION 'C'

ATMOSPHERIC AND VACUUM DISTILLATION OF 34·8° A.P.I. CRUDE



Distillate

% of crude	56·9
I.B.P., °F.	190
E.P., °F.	640

Gas oil

% of crude	15·6
Gravity, °A.P.I.	27·3
Flash, C.O.C., °F.	355
Visc., S.S.U. at 100° F.	75
Pour-point, °F.	60
Sulphur, %	2·03

Wax distillate 20

% of crude	13·2
Gravity, °A.P.I.	21·1
Flash, C.O.C., °F.	450
Visc., S.S.U. at 210° F.	54·4
Carbon residue, %	0·61
Pour-point, °F.	65
Sulphur, %	2·62

Wax distillate 50

% of crude	3·2
Gravity, °A.P.I.	17·1
Flash, C.O.C., °F.	545
Visc., S.S.U. at 210° F.	110
Carbon residue, %	3·36
Pour-point, °F.	45
Sulphur, %	3·06

Heavy wax distillate

% of crude	1·8
Gravity, °A.P.I.	14·8
Flash, C.O.C., °F.	595
Visc., S.S.U. at 210° F.	190·8
Carbon residue, %	5·78
Pour-point, °F.	45
Sulphur, %	5·78

Flux residue

% of crude	8·3
Specific gravity	1·061
Flash, C.O.C., °F.	645
Melting-point, °F.	117

Treated and filtered

Yield, %	88·0
Yield on crude, %	9·0
Gravity, °A.P.I.	28·1
Visc., S.S.U. at 100° F.	262
Visc., S.S.U. at 210° F.	51·2
Carbon residue, %	0·13
Pour-point, °F.	90
Sulphur, %	1·29

Furfural refining

Yield, %	77·6
Yield on crude, %	10·2
Gravity, °A.P.I.	27·0
Visc., S.S.U. at 100° F.	268
Visc., S.S.U. at 210° F.	51·3
Carbon residue, %	0·15
Pour-point, °F.	85
Sulphur, %	1·36

Furfural refining

Yield, %	69·5
Yield on crude, %	2·21
Gravity, °A.P.I.	24·6
Visc., S.S.U. at 210° F.	81·3
Carbon residue, %	0·61
Pour-point, °F.	85
Sulphur, %	1·68

Treated and filtered

Yield, %	84·7
Yield on crude, %	1·87
Gravity, °A.P.I.	26·0
Visc., S.S.U. at 210° F.	80·5
Carbon residue, %	0·48
Pour-point, °F.	75
Sulphur, %	1·63

S.A.E.-20
Ketone-benzol dewaxing

Yield, %	87·7
Yield on crude, %	7·88
Gravity, °A.P.I.	26·1
Flash, C.O.C., °F.	450
Visc., S.S.U. at 100° F.	348
Visc., S.S.U. at 210° F.	54·5
Carbon residue, %	0·18
Pour-point, °F.	—5
Viscosity index	93
Sulphur, %	1·47

S.A.E.-50
Ketone-benzol dewaxing

Yield, %	89·1
Yield on crude, %	1·67
Gravity, °A.P.I.	23·4
Flash, C.O.C., °F.	550
Visc., S.S.U. at 100° F.	1,112
Visc., S.S.U. at 210° F.	88·8
Carbon residue, %	0·52
Pour-point, °F.	0
Viscosity index	86·2
Sulphur, %	1·73

THE CRUDE OILS OF BAHREIN ISLAND

By J. R. KEITH

Manager, Research and Development Division, The Bahrein Petroleum Company Limited

Bahrein Island, the largest of the Bahrein group, is 30 miles long and 10 miles wide and is located in the Persian Gulf a few miles from the Arabian mainland. The Bahrein oilfield is located near the centre of the island and is 7½ miles long and 2½ miles wide, comprising approximately 16,000 acres.

The Bahrein field was discovered in 1932. Accumulative total production to 1 October 1946 was approximately 76,000,000 bbl. The optimum production rate has been established at about 20,000 bbl. per day. The majority of the field production is from the 'second-pay limestone' of the Bahrein Zone, the productive section being about 500 ft. in thickness and occurring between depths of 1,800 and 2,300 ft. on the crest of the structure.

Bahrein crude is an intermediate base crude, according to the U.S. Bureau of Mines system of classification. Light distillate products are predominantly paraffinic, having low octane numbers and high cetane numbers.

The yields and characteristics of typical fractions obtainable by distillation of Bahrein crude oil are shown in Table I. The data present an illustrative breakdown into a series of crude products. In actual refining practice, cut-points may deviate materially from those shown.

Bahrein crude oil may be refined to yield the whole range of petroleum products. Following is a brief discussion of the principal points of interest in regard to refining characteristics.

Gasoline

A 25 to 35% yield of straight-run gasoline is obtainable from Bahrein crude oil. The gasoline is low in octane number and contains some mercaptans which are readily removed by caustic washing or other processes.

The heavier fractions of straight-run gasoline respond well to thermal reforming, which may be used to attain a more satisfactory octane level. For example, the whole 360° end-point gasoline may be separated into a light cut of approximately 60-octane number and 200° F. end-point, and a heavier fraction. The light cut is suitable for either aviation or motor gasoline blending. By reforming the heavier cut, a gasoline of 68–72-octane number is readily obtainable.

Table I

Yields and Characteristics of Typical Crude Products obtainable by Distillation of Bahrein Crude Oil

		Gasolines (Propane-free)		*Kerosine after 360° F. E.P. gasoline*	*Light Diesel after kerosine*	*Residuum after light Diesel*	*Heavy gas oil after light Diesel*	*Lube. oil distillate after heavy gas oil*	*Asphalt after lube. distillate*
	Crude	*360° F. E.P.*	*437° F. E.P.*						
Yield to crude, vol. %	100·0	25·2	35·1	13·4	15·1	45·4	19·0	10·7	15·7
Cut to crude, start	0	0·9	0·9	26·1	39·5	54·6	54·6	73·6	84·3
end	100·0	26·1	36·0	39·5	54·6	100·0	73·6	84·3	100·0
Gravity, °A.P.I.	32·9	67·2	60·7	44·4	34·6	16·1	24·5	17·5	..
Specific gravity 60/60	..	..	..	..	..	..	..	..	1·042
Flash (C.T.), °F.	..	..	..	150	..	..	..	..	..
Flash (C.O.C.), °F.	..	..	..	..	..	..	..	460	..
Viscosity, S.S.U. at 70° F.	65	..	..	..	..	..	..	..	..
„ S.S.U. at 100° F.	50	..	..	..	40	..	105	..	..
„ S.S.U. at 130° F.	..	..	..	..	36	920	60	330	..
„ S.S.U. at 210° F.	..	..	..	..	..	133	39	70	..
„ Saybolt thermo at 60° F.	..	..	..	350	..	..	..	..	..
Pour-point, °F.	0	..	..	..	+20	+55	+60	+80	..
Reid vapour pressure	7·2	9·7	7·8	..	..	..	..	..	..
Sulphur, wt. %	2·0	0·020	0·054	0·20	1·3	3·5	2·4	3·4	4·8
Wax (Holde), %	2·0	..	..	..	..	..	..	..	..
Carbon residue (Conradson), %	..	..	..	..	..	8·7	..	..	..
Aniline point, °F.	..	..	..	143	156	..	..	..	..
Diesel index	..	..	..	..	54	..	..	..	..
Smoke-point, mm.	..	..	..	24	..	..	..	..	..
Octane number, C.F.R.M.	..	48·6	40·0	..	..	..	..	..	..
A.S.T.M. distillation, °F.:									
Initial	..	98	98	370	495	..	..	..	..
10% rec.	..	135	150	395	525	..	..	..	..
20% „	..	162	190	405	535	..	..	..	..
50% „	..	242	295	420	558	..	..	..	..
90% „	..	324	405	462	600	..	..	..	..
End-point	..	360	437	480	620	..	..	..	..
Penetration at 77° F.	..	..	..	..	..	..	..	..	56
Ductility at 77° F.	..	..	..	..	..	..	..	..	150+
Softening-point (B. and R.), °F.	..	..	..	..	..	..	..	..	124

The residuum remaining after removal of gasoline, kerosine, and gas oil is suitable charging-stock for thermal cracking. In a Dubbs two-coil unit a yield of about 45% of 66–8-octane number gasoline is obtained. By a combination of crude distillation, reforming and thermal cracking, an overall yield of 35% to 40% of gasoline of about 67-unleaded octane number is obtainable from Bahrein crude oil.

Kerosine

Kerosine distillate yields up to about 20% are obtainable from Bahrein crude oil. The raw distillates are of relatively high burning quality in spite of an aromatic content of 15 to 20%. Sulphur dioxide refining, with moderate dosages, yields illuminating kerosines of exceptionally good burning quality. Smoke-points (I.P.) up to 45 mm. are easily obtainable.

Diesel Oils

High-quality automotive and industrial Diesel oils are obtainable from Bahrein crude oil. The cetane numbers of these products are exceptionally high. A relatively high wax content in the heavier fractions limits their use when low pour-points are necessary. The heavy waxy gas-oil fractions are desirable charging-stocks for either thermal or catalytic cracking.

Lubricating Oils

Either residuum or distillate from Bahrein crude oil may be processed for the production of high-quality lubricating oils. An appropriate combination of deasphalting, solvent refining, and dewaxing results in the production of 90–100 V.I. oils for excellent quality. 60 to 70 V.I. oils are produced from distillate cuts by light acid treatment and dewaxing.

Asphalts

Vacuum reduction of Bahrein residua results in the production of typical steam-refined asphalts. The yield is 15 to 18% to crude. These products are very high in ductility and are relatively susceptible to temperature changes. Higher yields of less temperature-susceptible asphalts may be produced by air-blowing appropriate residua. Asphalts produced from Bahrein crude oil are exceptionally resistant to oxidation and possess other characteristics indicative of superior performance in paving or industrial application.

THE CRUDE OILS OF THE MIDDLE EAST

By D. A. HOWES and L. C. STRANG

Anglo-Iranian Oil Company Limited

By the end of 1946 the Middle East was firmly established as the second largest oil-producing area outside the United States. The crude-oil output of the region totalled 779,000 bbl. daily, being exceeded only by Venezuela with an output of 1,100,000 bbl. daily.

At the close of 1946 the daily output of the area and the refinery capacities have been stated to be as follows [6, 1946]:

Middle East Field Operations

Company and Middle East headquarters	*Location of concession*	*No. of active fields*	*No. of active wells*	*Production bbl. daily*
Anglo-Iranian Oil Co. Ltd., Abadan, Iran . . .	Iran	6	64	422,000
Arabian American Co., Dhahran, Saudi Arabia .	Saudi Arabia	1	40	173,000*
Bahrein Petroleum Co. Ltd., Bahrein Island. . .	Bahrein Island	1	62	23,000
Iraq Petroleum Co. Ltd., Haifa, Palestine, and Kirkuk, Iraq	Iraq	2†	11†	96,000
Kuwait Oil Co. Ltd., Kuwait	Kuwait	1	5	40,000
Anglo-Egyptian Oilfields Ltd., Cairo . . .	Egypt	2	100	25,000
Petroleum Development (Qatar) Ltd., Manama, Bahrein Island . .	Qatar	1‡	2‡	Nil
Total		14	284	779,000

* Production in late December 1946: 200,000 bbl. daily.

† Includes one well of Anglo-Iranian Oil Co. Ltd. in the Naft Khaneh field, producing 6,000 bbl.

‡ Wells shut in.

Refineries of the Middle East

Company and plant location	*Capacity, bbl. daily*	
	Crude oil	*Cracking*
Anglo-Iranian Oil Co. Ltd., Abadan, Iran	400,000	125,000
Kermanshah Petroleum Co. (Anglo-Iranian), Kermanshah, Iran	2,300	..
Khanaqin Oil Co. (Anglo-Iranian), Alwand, Iraq	6,000	..
Arabian-American Oil Co., Ras Tanura, Saudi Arabia	90,000	..
Bahrein Petroleum Co. Ltd., Bahrein Island	110,000	29,000
Consolidated Refineries Ltd., Haifa, Palestine	84,000	33,000
Anglo-Egyptian Oilfields Ltd., Suez, Egypt	35,000	6,500
Egyptian Government, Suez, Egypt . .	1,750	..
Total	729,050	193,500

Estimated reserves proved by drilling, in the Middle East, in January 1946, have been assessed by Logan as follows [4, 1946]:

Country	*Estimated proved reserves (thousands of bbl.)*
Iran	6,000,000
Iraq	4,750,000
Kuwait . . .	4,000,000
Saudi Arabia .	3,000,000
Qatar . . .	500,000
Bahrein Island .	250,000
Egypt . .	75,000
Total . . .	18,575,000

In the opinion of the United States Technical Oil Mission to the Middle East (DeGolyer Mission) [2, 1944] the above estimate may reasonably be increased by 10 billion barrels by including, along with the reserves proved by developed fields, the reserves indicated by fields discovered but not fully explored.

Iran

The principal oilfields of Iran and their present production (1946) are as follows [6, 1946]:

Name of field	*Year of discovery*	*No. of producing wells*	*Producing depths, ft.*
Masjid-i-Sulaiman . .	1908	27	2,000–3,000
Haft Kel	1928	23	3,000–4,000
Naft-i-Safid	1934	1	5,700
Gach Saran	1928	3	4,000–7,000
Agha Jari	1937	8	6,000–9,000
Pazanun	1937	..	6,000–8,000
Naft-i-Shah	1923	2	2,600–2,700
Total	..	64	..

All the above wells are flowing and the fields are operated by the Anglo-Iranian Oil Co. Ltd.

The producing formation is the Asmari limestone of Lower Miocene and Upper Oligocene age.

Although there are some differences, the general nature of the oil does not vary greatly throughout the country, apart from that from the Pazanun field which is a condensate. The oils are of mixed base, predominantly paraffinic, and are all classed as 'Intermediate-Wax Bearing' by the U.S. Bureau of Mines Method [11, 1935].

The oils are associated in the field with large volumes of gas held in solution under high pressures which range from 1,500 lb./sq. in. downwards. By careful reservoir control an entirely water-free crude is produced, with gas production limited strictly to solution gas. With the exception of Masjid-i-Sulaiman, the major fields (i.e. Haft Kel, Agha Jari, and Gach Saran) incorporate the multistage principle of stabilization for the crude oil [7, 1945]. The oil passes through six or seven stages, the pressure being progressively lowered at each stage releasing gas, the last stage being operated at 10 lb./sq. in. gauge or atmospheric pressure according to the degree of stabilization required. At Gach Saran representative pressures of the stages are 1,200, 700, 120, 44, 26, 13, and zero lb./sq. in. gauge pressure. The gas released consists of the paraffinic light hydrocarbons with some hydrogen sulphide and carbon dioxide. At Haft Kel, for example, the total combined gas evolved from the seven stages is as follows:

	%
H_2S and CO_2 . . .	4·2 vol.
Methane . . .	75·8 „
Ethane . . .	10·6 „
Propane . . .	5·8 „
Butanes . . .	2·5 „
Heavier . . .	1·1 „

The crude processed in Abadan refinery is stabilized in the multistage separators in the fields, usually with the last stage operating at 10 lb./sq. in. gauge pressure and 80° F. The crude oil therefore retains some of the above gases in solution so that further quantities are released on distillation of the oil. The butanes and pentanes in this gas are, of course, recoverable as natural gasoline by conventional processes of compression and stabilization, while the lighter gases are used as refinery fuel.

Inspection data on the crude oils from the various Iranian fields are as follows:

Field	*M.-i.-S. and Haft Kel*	*Agha Jari*	*Gach Saran*	*Naft-i-Shah*
Sp. gr. at 60° F. . .	0·836	0·844	0·861	0·810
Distillation at 50° C. .	drops	1	drops	2·5
„ 75° C. .	4	4	4	3·5
„ 100° C. .	9·5	8	8	8·5
„ 125° C. .	17	12·5	13	15·5
„ 150° C. .	23	18	18	24
„ 175° C. .	28	24	23	32·5
„ 200° C. .	34	28·5	27	38·5
„ 225° C. .	39	33	31	44
„ 250° C. .	44·5	37·5	35·5	51
„ 275° C. .	50·5	43	40·5	55·5
„ 300° C. .	56	49	45·5	61·5
Sulphur, wt. % . . .	1·2	1·4	1·6	0·76
Viscosity at 70° F., cs. .	5·7	7·7	15·0	5·2
Hard asphalt, wt. % .	0·9	0·6	1·8	..
Water, vol. % . . .	Nil	Nil	Nil	Nil

Assessment of the above crude oils by means of Hempel Distillations (U.S. Bureau of Mines Bulletin 207) are summarized as follows:

Field		*Haft Kel*	*Agha Jari*	*Gach Saran*
Sp. gr. of sample at 60° F. . .		0·836	0·859	0·866
Light gasoline,	vol. %	10·1	9·2	9·7
Gasoline+naphtha,	„	33·6	30·8	28·2
Kerosine distillate,	„	11·5	10·0	9·0
Gas-oil distillate,	„	19·9	19·5	16·5
Non-viscous lub. distillate,	„	10·5	11·9	9·3
Medium lub. distillate,	„	3·2	2·1	3·4
Viscous lub. distillate,	„	..	..	..
Residue,	„	20·8	24·3	32·4
Loss,	„	1·5	1·4	1·3

The gasoline of about 150° C. end-point from the above crudes contains about 9% aromatic hydrocarbons (1% benzene, 3% toluene, and 5% xylenes and ethylbenzene), and the kerosine fraction about 17% aromatics. These aromatics may be extracted by appropriate selective solvents such as liquid SO_2. Both the gasoline and kerosine contain small amounts of alkyl mercaptans and sulphides and are refined by conventional means before marketing. Oxygen and nitrogen compounds are entirely absent from these distillates.

The essentially paraffinic nature of the above Iranian crude oils is illustrated by the low octane number of the gasolines (*c.* 50 C.F.R.M.M. for 185° C. end-point) and the high cetane number (*c.* 56) of the gas-oils. By superfractionation, however, valuable high octane number and rich mixture-rating components for aviation spirit ('isohexane' and 'isoheptane' cuts) may be obtained from the gasoline [1, 1946].

The lubricating-oil portion of the crude is waxy and of low viscosity index, but by conventional dewaxing, solvent extraction, and acid and clay treatments lubricants of 100 V.I. and good colour and stability may be obtained, varying in viscosity from light spindle oil to heavy cylinder stock.

Fuel-oil components may be prepared from the waxy residue remaining after removal of the gas-oil and lighter fractions by viscosity breaking or thermal cracking of the waxy distillate fraction.

Specification bitumens may be obtained by vacuum distillation to short residues, but low-penetration bitumens are more easily obtained by air-blowing bitumens of 200–300 penetrations.

Iraq

Present production in Iraq is as follows [6, 1946]:

Field	*Year of discovery*	*No. of producing wells*	*Producing depths, ft.*	*Average daily production, bbl.*
Kirkuk . .	1927	10	2,750	90,000
Naft Khaneh	1926	1	3,000	6,000

The Naft Khaneh crude is from the same field as the Naft-i-Shah field in Iran. The Kirkuk structure is about 60 miles long and 3 miles wide, and the producing formation 350–400 ft. thick [9, 1945]. The field is operated by the Iraq Petroleum Co. Ltd., and the production methods used ensure maximum conservation of the energy of the reservoir. This is a combination gas-cap water-drive type of structure and produces from the Quarah Chauk limestone in the Miocene–Oligocene. This highly porous limestone permits great freedom of oil movement and provides wells capable of very large rates of flow. All wells flow under natural reservoir pressure.

After two-stage gas separation at 75 and 50 lb./sq. in. the crude oil is processed through stabilizing columns to produce a crude oil containing about 2% butane and is then piped in 12-in. pipelines to Haifa and Tripoli for refining or shipment. At present additional 16-in. pipelines are being constructed to allow further production from this field.

In appearance Kirkuk crude oil is reddish-brown, without bloom, and transparent only in thin section. The following table gives the characteristics of the crude as determined by I.P. standard methods.

Sp. gr. at 60° F.	0·844
Distillation at 50° C. . . .	Trace
„ 75° C.	4·5
„ 100° C.	10
„ 125° C.	15
„ 150° C.	21
„ 175° C.	26·5
„ 200° C.	32
„ 225° C.	38·5
„ 250° C.	42·5
„ 275° C.	46·5
„ 300° C.	52·5
Sulphur, % wt.	2·0
Viscosity Redwood I., sec.:	
at 40° F.	59
at 70° F.	44·5
at 100° F.	38·5
Hard asphalt, % wt. . . .	0·9
Flash-point, °F.	Below 0° F
Pour-point, °F.	Below 0° F.
Chloride content, % wt. . . .	0·001

Assessment of the above crude oil by means of the Hempel Distillation (U.S. Bureau of Mines Bulletin 207) is as follows:

Light gasoline,	vol. %	11·3
Gasoline+naphtha,	„	32·8
Kerosine distillate,	„	15·7
Gas-oil distillate,	„	14·0
Non-viscous lub. distillate,	„	9·9
Medium lub. distillate,	„	2 6
Viscous lub. distillate,	„	..
Residue,	„	23·8
Loss,	„	1·2

This oil is a mixed-base crude, predominantly paraffinic, and is classed as 'Intermediate Wax-Bearing' by the U.S. Bureau of Mines Method [11, 1935].

The above figures show that apart from the higher sulphur content this crude is not very different from the Iranian crudes described above. It is of low specific gravity and low viscosity and is mobile down to very low temperatures.

The characteristics of raw products typical of those obtained at a refinery operating on Kirkuk crude are shown hereunder. In this case treatment in a light topping plant and stabilizing unit is followed by atmospheric distillation giving gasoline of different grades as overhead, with kerosine, gas-oil, and wax distillate sidestreams.

Typical examples are as follows:

	Light gasoline	*Heavy gasoline*	*Kerosine*	*Gas-oil*	*Residue*
% vol. on crude	12·3	11·3	15·4	20·5	40·8
Sp. gr. at 60° F.	0·6605	0·7355	0·788	0·842	0·950
Distillation:					
I.B.P. °C.	27	77	161	222	..
10% at °C.	37	104	170	247	..
50% at °C.	65	121	186	285	..
90% at °C.	97	136	218	352	..
F.B.P. °C.	105	154	234	374	..
Sulphur, wt. %	0·03	0·08	0·19	0·98	3·55
Pour-point	..	..	..	..	60
Viscosity at 100° F. Redwood I., sec.	..	..	..	..	1272

Alternative distillations of the crude have given the following yields and products [5, 1934].

	1				2	
	Gasoline	*Kerosine*	*Gas-oil*	*Wax distillate*	*Gasoline*	*Fuel oil*
Yield on crude, vol. %	21·2	26·3	12·2	21·9	26·8	71·2
Sp. gr. at 60° F.	0·705	0·800	0·852	0·903	0·724	0·899
Distillation: I.B.P. °C.	30	165	..	..	30	..
10% at °C.	61	177	..	..	71	..
50% at °C.	100	209	..	..	121	..
90% at °C.	138	270	..	..	162	..
F.B.P. °C.	166	300	..	..	190	..
Flash-point, °F.	..	118	235	300	..	186
Viscosity at 60° F. Redwood I., sec.	..	..	46	..	..	252
„ „ 100° F. „ „ „	..	..	..	115	..	90
„ „ 140° F. „ „ „	..	..	..	59	..	..
Sulphur, wt. %	..	..	1·16	..	..	2·44
Pour-point, °F.	..	..	25	80	..	80
Calorific value, B.Th.U./lb.	..	..	19,620	..	..	19,206

Straight-run gasolines are lower in aromatic content than Iranian gasolines, and 185° C. end-point gasoline has an octane number (C.F.R.M.M.) less than 50. Satisfactory kerosines may be obtained from the raw kerosines by solvent refining with liquid SO_2. Gas-oils are of excellent quality, having high cetane numbers and satisfactory viscosity and pour-point characteristics. Satisfactory lubricating oils are obtained by conventional dewaxing, solvent refining, and acid and clay finishing treatments. Commercial grades of paraffin wax may be obtained by conventional means from wax distillates. Suitable fuel oils may be produced by blending back the atmospheric distilled residues with gas-oil or kerosine, or by subjecting such a residue or a vacuum distillate from it to thermal-cracking processes. Specification bitumens may also be obtained by vacuum distillation to short residues or by air-blowing such short residues.

There are five additional productive structures in Iraq, most of which have been tested only by one or two wells. The Ain Zalah field is one of these, the crude being similar to that from Kirkuk. The presence of a high-gravity high-sulphur content reserve has been established at Qaiyarah, but the oil is not at present refinable and no plans have been made for its development.

Bahrein Islands and Saudi Arabia

These crudes are conveniently considered together as the fields are jointly controlled (1946) by Standard Oil Co. of California and the Texas Co. Both crudes are refined at Bahrein refinery, while Saudi Arabia crude is also refined at Ras Tanura as well as shipped elsewhere. Data on the principal fields and their present production [6, 1946] are as follows:

Name of field	*Year of discovery*	*No. of producing wells*	*Producing depth, ft.*	*Daily average production bbl.*
Bahrein Islands	1932	62	2,000–2,500	23,000
Saudi Arabia				
Dammam	1935	31	4,700	100,000
Abu Hadriya	1940	1	10,200	Shut in
Abqaiq	1940	6	6,500	70,000
Qatif	1945	1	7,500	3,000

All the above wells are flowing. The producing formations are all limestone. The crude passes through two separators, and then through gas traps to a weathering column. The vapour from the weathering operation passes to the stage gas compressors and then to the gas rectifier. This operation completes the stabilization of the crude and gives a maximum recovery of light hydrocarbons.

The above crudes are very similar to other Middle East crude oils, being intermediate-base type, predominantly paraffinic, and of high sulphur content.

Analyses of fractions obtained from Bahrein crude by a Hempel distillation are as follows:

Fraction	Crude oil	Gasoline end-point				116–182° C. naphtha	182–274° C. kerosine	Residues			
		117° C.	148° C.	177° C.	204° C.			Above 148° C.	Above 177° C.	Above 205° C.	Above 274° C.
Yields, vol. % on crude	100·0	9·7	16·5	22·7	29·6	13·5	17·4	83·3	77·1	70·2	59·1
Properties of fractions											
Gravity, °A.P.I.	31·9	81·7	74·5	68·0	62·7	58·4	44·5	25·7	24·1	22·0	18·9
Sp. gr. at 60° F.	0·8660	0·6637	0·6869	0·7093	0·7256	0·7451	0·804	0·9001	0·9094	0·9218	0·9408
Distillation: I.B.P., °C.	55	27	32	35·5	40·5	89·5	182	161	193	228	281
5% at °C.	95·5	33	45·5	52	58	107	190	182	215	250	297
10% at °C.	122	39	52	61	70	112	194·5	198	227	264·5	310·5
20% at °C.	170	46·5	63	76	88	118	200	235·5	261	292	334
30% at °C.	220·5	53	72	89	104·5	124	205	279	300	322	349
50% at °C.	325·5	66	89	111	133	135	216	348	358	361	365
70% at °C.	378	81	104·5	130·5	156	147	240	366	374·5	374	378
90% at °C.	397	102	125	153	183	165	252	388	390·5	..	..
F.B.P., °C.	398	117	148	177	205	183	274	388	390·5	390·5	390·5
Total distillate, %	94	96	97	97·5	98	99	99	93·5	93·0	92·5	91·5
Residue	..	1	1	1	1	1	1	..	..	..	..
Loss	..	3	2	1·5	1	0	0	..	..	..	..
Vol. % at 204° C.	27·5	..	..	..	..	..	29	12	2·5	..	..
Vol. % at 300° C.	45·5	..	..	..	..	..	..	35·5	30·0	23	6
Sulphur, wt. %	2·0	0·015	0·02	0·02	0·03	0·03	..	..	..	2·74	3·22
Octane no. (C.F.R.M.M.)	..	64	55	48	42	36	..	..	..	..	..
Flash-point (P.M.), °F.	..	..	..	..	..	..	..	..	..	226	268
Viscosity (Furol), sec. at 122° C.	..	..	..	..	..	..	..	..	..	19	335
B.S. and W., %	0.2	..	..	..	..	..	..	..	..	0·1	0·1
Cold test, ° F.	< 0	..	..	..	..	..	..	..	..	15	20

Assessment of Dammam crude by means of the Hempel distillation (U.S. Bureau of Mines Bulletin 207) is summarized as follows:

Sp. gr. of sample		0·852
Light gasoline,	vol. %	8·0
Gasoline+naphtha,	„	30·0
Kerosine distillate,	„	11·8
Gas oil distillate,	„	21·8
Non-viscous lub. distillate,	„	11·4
Medium lub. distillate,	„	4·4
Viscous lub. distillate,	„	..
Residue,	„	20·4
Loss,	„	0·7

Typical analyses of the Bahrein and Arabian crude oils processed at Bahrein Refinery [8, 1945] are as follows:

Crude	Bahrein	Arabian
Gravity, °A.P.I.	33·2	34·7
Sp. gr. at 60° F.	0·859	0·851
Sulphur, wt. %	2·21	1·75
Viscosity, S.S.U. at 100° F.	58·5	42·7
Pour-point, °F.	20	10
Sediment and water, vol. %	0·1	Trace to 0·1
225° C. end-point gasoline		
Yield, vol. %	37·4	37·2
Octane no. (C.F.R.M.M.)	40	37
Residue above 225° C.		
Yield, vol. %	62·0	62·0
Gravity, °A.P.I.	20·0	24·9
Sp. gr. at 60° F.	0·934	0·905

The products from the crude distillation units are light and heavy gasoline, kerosine, gas oil, and residual fuel oils. Part of the residue is also vacuum distilled to obtain intermediate and heavy gas oil fractions which are used as charging stock for catalytic cracking operations. The light gasoline is used in the blending of finished gasolines, while the heavy gasoline or naphtha is the charging-stock for reforming operations. The kerosine is treated by SO_2 extraction. The residual fuel is marketed as fuel oil or used as charging stock for thermal cracking operations.

Kuwait

The Burgan oilfield in the independent Sheikhdom of Kuwait was discovered in 1938 and production began in mid-1946. Production at present is from five flowing wells at 3,800–4,400 ft. [6, 1946]. As distinct from the other Middle East oilfields, which are in limestone formation, the Kuwait production is from Middle Cretaceous sandstones and the oil is being produced from two sands. The field is jointly operated by the Anglo-Iranian Oil Co. Ltd. and the Gulf Oil Corp.

After gas separation in the field, the oil is piped to a marine terminal at Fahahil on the Persian Gulf.

The oil is similar to other Middle East oils in being of intermediate-base type, predominantly paraffinic, and of high sulphur content. Typical analyses of oil from the two producing sands are as follows:

Producing sand	First	Third
Sp. gr. at 60° F.	0·8595	0·862
Distillation at 50° C., vol. %	Nil	Drops
„ „ 75° C., „	2·5	4
„ „ 100° C., „	6·5	7·5
„ „ 125° C., „	11	12
„ „ 150° C., „	16	17
„ „ 175° C., „	21	22
„ „ 200° C., „	25·5	26
„ „ 225° C., „	30	31
„ „ 250° C., „	34·5	35·5
„ „ 275° C., „	39·5	40
„ „ 300° C., „	44·5	44·5
Sulphur, wt. %	2·0	2·2–2·5
Viscosity at 70° F., cs.	13·4	13·7
Hard asphalt, wt. %	0·8	0·8
Water, vol. %	Nil	Nil

Assessment by means of Hempel distillations (U.S. Bureau of Mines Bulletin 207) are summarized as follows:

Producing sand		First	Third
Sp. gr. at 60° F.		0·8595	0·860
Light gasoline,	vol. %	8·7	9·1
Gasoline+naphtha,	„	28·7	28·7
Kerosine distillate,	„	9·5	8·3
Gas oil distillate,	„	16·4	16·6
Non-viscous lub. distillate,	„	10·8	9·5
Medium lub. distillate,	„	3·1	3·6
Viscous lub. distillate,	„	..	..
Residue,	„	31·0	31·9
Loss,	„	0·5	1·4

In spite of the high sulphur content of the above crude, the gasoline fractions are very low in sulphur content and require only light refining treatments.

Qatar

Oil was discovered at Dukhan in the peninsula of Qatar (Persian Gulf) in 1940. Two wells were drilled at 5,800–6,000 ft. in the Kerkrit limestone. The crude oil is similar in nature to other Middle East crude oils, being of intermediate type, predominantly paraffinic, and of high sulphur content. Typical analyses are as follows:

Sp. gr. at 60° F.	0·854
Distillation at 75° C., vol. %.	1·5
„ „ 100° C., „ .	6
„ „ 125° C., „ .	11·5
„ „ 150° C., „ .	17
„ „ 175° C., „ .	22·5
„ „ 200° C., „ .	29
„ „ 225° C., „ .	35
„ „ 250° C., „ .	41
„ „ 275° C., „ .	46
„ „ 300° C., „ .	52
Sulphur content . . .	1·90
Hempel distillation	
Gasoline + naphtha, vol. % .	31·5
Kerosine distillate, „ .	10·0
Gas oil distillate, „ .	17·0
Residue, „ .	41·0
Loss, „ .	0·5

Egypt

The principal oilfields of Egypt and their present production [1, 1946] are:

Field	*Year of discovery*	*No. of producing wells*			*Producing depth, ft.*	*Daily average production, bbl.*
		Flowing	*Gas lift*	*Pumping*		
Hurghada .	1913	..	..	62	1,700–2,200	1,000
Ras Gharib .	1938	25	13	..	1,500–2,400	24,000
Sudr . .	1946	..	..	..	2,675–2,826	Discovery
Gemsah .	1908	1	..	..	1,240–1,310	Suspended
Abu Durba .	1918	..	..	27	300–1,500	Suspended

Of these fields Gemsah and Abu Durba are now regarded as exhausted and nearly all the production is from the Ras Gharib field.

The Hurghada field is in the Nubian sandstone, and production is difficult due to the presence of water. The current output, in fact, is 93% water [10, 1945]. The Ras Gharib field is in the Basal Miocene limestone and Premiocene sands and owing to war emergencies the rate of production has undoubtedly been too high for efficient operation. These fields are all operated by the Anglo-Egyptian Oil Co. Ltd.

The oils from these fields differed very considerably from each other as follows [3, 1923]:

	Abu Durba	*Gemsah*	*Hurghada*
Sp. gr. at 15° C. . . .	0·945–0·960	0·827	0·907–0·925
Viscosity at 100° F. Redwood I., sec.	c. 3,000	..	c. 400
Sulphur, wt. % . . .	2·35	0·65	2·2–5·0
Asphalt (% insol. in pentane) .	10·5	0·63	10–11
Paraffin wax	..	4·94	7–8

The Ras Gharib crude oil has a specific gravity at 60° F. of 0·898–0·904.

Hurghada crude oil gives the following yields of products:

	Crude oil	*Gasoline*	*Kerosine*	*Gas oil*	*Residue*
Yield on crude, wt. %	100·0	12·5	7·5	16·0	64·0
Sp. gr. at 15°/4° C. .	0.900	0 722	0.808	0.850	0.960
Distillation:					
I.B.P., °C. . .	..	35	170	..	..
10% at °C. . .	..	64	190	..	..
50% at °C. . .	..	110	220	..	..
90% at °C. . .	..	155	250	..	..
F.B.P. at °C. .	..	178	275	..	..
Sulphur, wt. % .	2·8	0·08	0·15	1·3	..
Viscosity at 100° F. Redwood I., sec. .	..	..	..	35	170
Pour-point, °F. .	< 32	..	..	25	90
Carbon-residue (Conradson) . .	..	..	..	..	7·5

This crude is a typical mixed-base crude, and differs from other Middle East crudes in having a higher gravity and lower gasoline contents. It has a high paraffin wax and bitumen content.

During the war the Suez refinery processed approximately 28,000 bbl. of crude daily, meeting all requirements for treatment of indigenous oil. Discovery of new reserves is regarded as of paramount importance and an active exploration is under way.

REFERENCES

1. BIRCH, S. F., DOCKSEY, P., and DOVE, J. H. *J.I.P.* **32**, no. 268, 167 (1946).
2. DeGolyer Mission. American Association of Petroleum Geologists Bulletin, July 1944.
3. GUTHRIE, W. A. *J.I.P.T.* **9**, 212 (1923).
4. LOGAN, L. J. *Oil Weekly*, **122**, no. 1, 20 (1946).
5. *Oil and Gas J.* **33**, no. 23, 12 (1934).
6. Ibid. **45**, no. 34, 187 (1946).
7. WILLSON, C. O. Ibid. **44**, no. 22, 74 (1945).
8. —— Ibid. no. 24, 110 (1945).
9. —— Ibid. no. 27, 60 (1945).
10. —— Ibid. no. 31, 62 (1945).
11. U.S. Bureau of Mines, R.I. 3279 (1935).

EVALUATION OF CRUDE OILS AND OIL STOCKS

By W. L. NELSON

University of Tulsa

Introduction

THEORETICALLY it is possible to produce any type of refined product from any crude oil, but it is not usually economically sound to do so. In a few instances the demand for a particular type of product or the elimination of a low-value one has been so insistent that major conversions of a chemical nature have been adopted. Among these are thermal cracking for reducing the yield of fuel oil, catalytic cracking for producing engine fuels of superior detonation quality, polymerization of cracking still gases for the elimination of excess gaseous fuel, and to a lesser degree solvent-extraction processes for separating unsuitable kinds of hydrocarbons from lubricating oils, Diesel fuel oils, and petroleum solvents. Nevertheless, the inherent quality or composition of a crude oil is of profound economic importance. The processing of an inherently inferior crude oil involves costly processing equipment and relatively small yields of the more valuable products.

It is common practice for the refiner to examine available crude oils with respect to:

1. Base or general properties.
2. Sulphur, emulsions, and salt, which cause general difficulties in processing.
3. Plant operating conditions. Primarily this necessitates a laboratory scale fractionating or true boiling-point distillation [29, 1938] curve, an equilibrium flash vaporization curve [29, 1938], and at least a curve of the specific gravity (or A.P.I.) of each fraction distilled.
4. Curves of the properties of the most promising products versus the percentage or yield of these products. Among the more common property curves are:
   (*a*) Viscosity of lubricating-oil fractions.
   (*b*) Octane number.
   (*c*) Aniline point of solvent, kerosine, and Diesel fuel fractions.
   (*d*) Penetration of asphaltic residues.
   The extent of such analyses ranges from 2- or 3-litre laboratory distillations to pilot-scale operations on 10-gallon quantities [30, 1935], and perhaps several such distillations are required.
5. Finished products. After having established the general properties and yields by means of the property curves of (4) and exploring the economy of various break-ups of the crude oil, most refiners feel it is necessary to actually produce finished products in quantity large enough to determine all of the commonly specified routine test properties. Batch or other semi-plant scale stills are employed and such details as chemical treatment, susceptibility to tetraethyl lead, pour-point, &c., may be explored.

Evaluations are Approximate

So many combinations of yields are possible in processing a crude oil, and market demands so frequently alter the quality or value of various products, that evaluation methods must be general and flexible. They must be generally useful so that current changes in the desirability of stocks can be followed almost day by day. Small refiners are particularly adept at altering their plant processing to take advantage of changes in the marketability of various products. Thus somewhat unscientific methods of evaluation are tolerated because their use involves less danger of error than to rely upon a single elaborate break-up of the crude oil which at no time faithfully represents the market situation. Nevertheless, the somewhat gross methods outlined here must always be used with caution and they should be augmented at the first opportunity by more complete tests.

Indexes, Factors, and Constants

Values of some of these indexes for the common bases of crude oils are summarized in Table IV.

The most widely useful index is the Characterization Factor of Watson and Nelson [35, 1933]. It was originally defined as:

$$K = \frac{\sqrt[3]{T_B}}{S},$$

in which T_B is the average molal boiling-point (°F. absolute) and S is the specific gravity at 60° F., but it has now been related to viscosity, aniline point, molecular weight, critical temperature, percentage hydrogen, &c., so that almost any available laboratory data can be used to estimate the characterization factor. Its primary value lies in the fact that it has been related to many properties both of a chemical and of an engineering nature. Typical characterization factors are [5, 1936]:

Pennsylvania stocks	12·2–12·5
Mid-Continent stocks	11·8–12·0
Gulf Coast stocks	11·0–11·8
Cracked gasoline	11·5–11·8
Cracking plant combined feeds	10·5–11·5
Recycle stocks	10·0–11·0
Cracked residuum	9·8–11·0

Table I indicates the characterization factors of particular stocks.

TABLE I

Characterization Factors of Miscellaneous Stocks

Stock	*A.P.I. gravity*	*Characterization factor*
Liquid paraffin hydrocarbons	..	12·7
Propane	146·2	14·7
Hexane	81·1	12·8
Octane	68·8	12·7
Raw absorption gasoline	94·6	13·6
Natural gasoline, Kettleman Hills	81·9	12·7
„ „ Mid-Continent	82·2	12·8
Mid-Continent distillates	24·9–47·2	11·8–12·2*
Smackover, Arkansas distillates	21·0–33·1	11·35–11·5*
Distillates from residues in cracking M.C. gas oil	12·6–21·4	10·25–10·7*
Distillates from residues in cracking M.C. gas oil	2·1–8·7	9·9–10·3*
Pennsylvania distillates	31·9–43·4	12·1–12·5*
Pennsylvania lube oil	28·0–30·3	12·3–12·5*
Cracked residuum	2·6–10·3	10·5–10·7*
„ „	−4·3	9·5
Benzene	..	9·8
Catalytic cracked naphtha, 300–400° F.	35·9	11·1

* Reference [36, 1935].

TABLE I (*cont.*)

Stock	*A.P.I. gravity*	*Characterization factor*
Cracked naphthas, M.C.	58·5–61·2	11·8–12·0
Pressure gas oil, paraffinic charge	32·0	11·8
„ „ „ naphthenic charge	26·6	11·2
Light cycle gas oil	20·0	10·5
Heavy cycle gas oil	11·0–14·0	10·4–10·5
East Texas crude oil	40·8	11·9
Mt. Pleasant, Mich. crude oil	43·3	12·0
Muskegon, Mich. crude oil	38·2	11·6
Kettleman Hills, Cal. crude oil	34·5	11·4
Signal Hill, Cal. crude oil	29·6	11·1
Venice, Cal. crude oil	22·5	10·9
Huntington Beach, Cal. crude oil	13·3	10·8
Peruvian crude oil	38·8	11·7
Bright stock, California	18·8	11·7

Other significant factors and constants are:

1. **Viscosity Index.** This index is a series of numbers ranging from 0 to 100 which indicate the rate of change of viscosity with temperature [4, 1938]. Typically paraffinic lubricating oils exhibit a V.I. of about 100 whereas naphthenic oils worse than those regularly marketed have a V.I. of zero. Thus a V.I. of 100 indicates an oil that does not become viscous at low temperatures nor become thin at elevated temperatures.

2. **Viscosity Gravity Constant.** This constant [4, 1938] involves gravity as well as viscosity, as:

$$\text{V.G.C.} = \frac{10G - 1{\cdot}0752\log(V-38)}{10-\log(V-38)},$$

in which G is specific gravity at 60° F. and V is viscosity at 100° F. in seconds Universal Saybolt. Typical values of the constant are shown in Table II.

TABLE II

Viscosity Gravity Constants of Crude Oils [8, 1931]

Paraffinic	
Pennsylvania	0·8067
Milltown, Pa.	0·800
Buckeye, Ohio	0·800
Eureka, Pa.	0·804
Paraffin Intermediate	
Ranger, Texas	0·827
Burbank, Okla.	0·828
Salt Creek, Wyoming	0·829
Reagon County, Texas	0·839
Seminole, Okla.	0·844
Mid-Continent	0·8367
Others	
Gulf Coast No. 1	0·8635
Van Zandt County, Texas	0·852
Light Mexican	0·860
Gulf Coast No. 2	0·8845
Heavy Mexican	0·894
Gulf Coast No. 3	0·9025
Sour Lake, Texas	0·916

3. **Aniline Point.** This is significant as an indication of aromaticity. The solvent properties of naphthas, the ignition quality of Diesel fuels, and the smoking or coking qualities of distillate fuel oils are related to the aniline point. High values indicate paraffinic properties whereas low values indicate the properties of aromatic hydrocarbons.

4. **Smoke Point.** The I.P.T. Smoke Point Test, Serial Designation K.36, is related to the height of flame that can be maintained with a kerosine without smoking and to its illuminating power [10, 1927]. According to Minchin [12, 1931] the smoke-points of hydrocarbons are about 73 mm. for paraffins, 24 mm. for naphthenes, and 7·5 mm. for aromatics.

5. **Diesel Index.** The ignition quality of Diesel fuel oils can be judged most easily by the Diesel Index:

$$\text{D.I.} = \frac{\text{Aniline pt. (°F.)} \times \text{gravity (A.P.I.)}}{100}.$$

A high D.I. (50–70) indicates good ignition quality, a value of 40 is considered suitable, and a value of 20 is inadequate for nearly all engines. The approximate relation of D.I. to other common properties and indexes is indicated in Table III.

TABLE III

Approximate Relation of Diesel Fuel Oil Constants to one another

Cetane no. (delay method)	*Diesel Index*	*Blending octane no.*	*Boiling-point gravity constant**	*Characterization factor*
30	19	51	201	11·15
35	27	43	196	11·34
40	37	35	191	11·53
45	45	27	187	11·69
50	53	19	183	11·85
55	59	11	180	11·97
60	65	2	178	12·06

* $G = B + (68 - 0{\cdot}703\,B)\log T$, in which B is the constant, G is A.P.I. gravity at 60° F., and T is 50% boiling-point, °C. [9, 1935].

There are numerous other indexes or constants which are not widely useful. Among these are: (1) Carbon-hydrogen ratio, (2) Parachor which involves surface tension and gravity [7, 1935], (3) the Correlation Index of the U.S. Bureau of Mines [31, 1940], Boiling-point Gravity Constant [9, 1935], and Characterization Gravity [13, 1941].

Base of Crude Oil

The classification of crude oils according to 'base' as practised extensively in the United States is inadequate, but long usage has given some meaning to the term and when used or defined with respect to various indexes, properties, &c., the retention of a classification by base is justified. The U.S. Bureau of Mines [11, 1935] classifies crude oils broadly by means of Key Fractions No. 1 and No. 2 which distil respectively at 482–527° F. at atmospheric pressure and 527–572° F. at 40 mm. pressure in the Standardized Bureau of Mines Hempel Distillation. In naming the crude oil, the first name designates the general properties of the gasoline or low-boiling part of the crude oil as determined by Key Fraction No. 1, and the second name applies primarily to the lubricating oil or high-boiling part of the crude oil as indicated by the gravity of Key Fraction No. 2. The presence of wax is determined by noting the cloud-point of Key Fraction No. 2. If the cloud-point is below 5° F. it indicates little wax and the crude oil is designated as 'wax free'. Accordingly the commonly classified crude oils are:

Base of crude oil		*A.P.I. gravity at 60° F.*		
Light fraction	*Heavy fraction*	*Key Fract. No. 1*	*Key Fract. No. 2*	*Approximate* charact. factor*
Paraffin		40 or more	30 or more	12 and higher
Paraffin	Intermediate	40 or more	20–30	..
Paraffin	Naphthene	40 or more	20 or lower	..
Intermediate	Paraffin	33–40	30 or more	..
Intermediate		33–40	20–30	11·4–12·0
Intermediate	Naphthene	33–40	20 or lower	..
Naphthene		33 or lower	20 or lower	11·4 and lower
Naphthene	Intermediate	33 or lower	20–30	..
Naphthene	Paraffin	33 or lower	30 or more	..

* Computed figures. Not stated by Bur. of Mines.

Table IV shows significant properties, indexes, constants, &c., of the various bases of crude oils. A major disadvantage of any crude-oil name system is the tendency to imbue the crude oil with all of the attributes of that class. Careful examination of Table IV forcefully indicates that wide ranges of properties are possible in each base of crude oil and that classification is not complete until several or perhaps all of the indexes and properties have been investigated.

TABLE IV

Comparison of the Evaluation Properties of Crude Oils

										Lubricating oils			
	Crude oils		*Gasoline (400 E.P.)*		*Solvents*	*Kerosine*		*Diesel fuel*				*Average viscosity, Saybolt Univ. seconds*	
Base of crude oil or source of stock	*Charact. factor*	*Viscosity gravity constant*	*A.P.I. gravity*	*A.S.T.M. Oct. no.*	*Aniline point, °F.*	*A.P.I. gravity*	*I.P.T. smoke point, mm.*	*Aniline point, °F.*	*Diesel index*	*A.P.I. gravity*	*Viscosity index*	*at 100° F. of a 700° F. b.p. fraction*	*at 210° F. of a 900° F. b.p. fraction*
Paraffin .	12·0–12·5	0·8–0·82	62–72	34–53	120–175	44–50	30–40	176–190	51–76	23–32	90–106	62	60
Intermediate .	11·8–12·0	0·82–0·85	54–64	50–61	105–165	45	18–30	160–176	49–65	28	65–85	75	75
Naphthene	11·0–11·5	0·85–0·9	48–55	55–71	65–130	29–39	12–24	115–150	up to 40	14–25	0–55	115	180
Thermal cracked .	10·0–11·8*	..	55–61	63–70	..	23–37	..	..	23–40	..	..	..	..
Coal-tar products .	9·5–9·8†	..	23–30†	90 up†	..	under 10†	..	below 68†	..	..	..	..	..

* Characterization Factor is not a constant for cracked stocks. See Table I. † Approximate and only for comparison.

Our knowledge of the chemical behaviour of the high-boiling hydrocarbons is still inadequate for much practical application, but Fig. 1 is offered [14, 1944] in an attempt to connect chemical composition with base of crude oil. Note that a fourth major base, i.e. aromatic or benzenoid, is introduced in Fig. 1. Aromatic crude oils are uncommon in the United States but are found in some regions, notably Burma and Borneo [28, 1944].

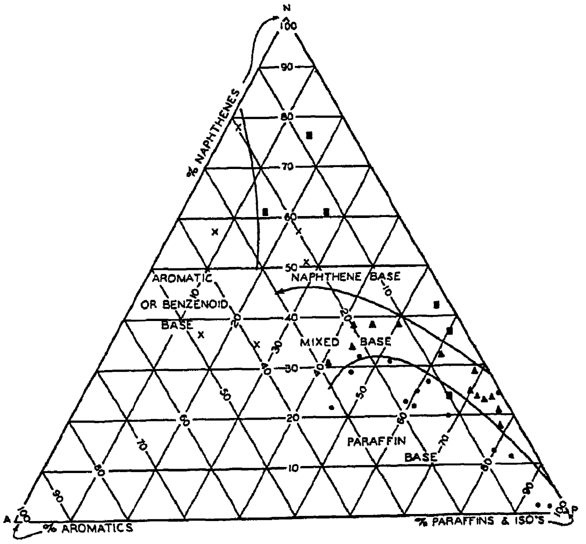


FIG. 1. Approximate hydrocarbon analyses of crude petroleums. (Courtesy of *Oil and Gas Journal.*)

Sulphur, Salt, and Emulsions

Sulphur not only is deleterious in many finished products but is a source of great expense in refinery processing because of corrosion. Equipment costs rise mainly because of the need for high-chromium steels [15, 1944]. In addition to the standard methods of determining total sulphur, the amount of hydrogen sulphide that a crude oil or stock will evolve during processing can be judged by means of the Davis, Jones, and Neilson method [3, 1938] of steam distillation by which hydrogen sulphide and hydrochloric acid (from brine associated with the crude oil) are liberated and collected in suitable chemical reagents. The amount of sulphide and acid evolved is not directly related to the total sulphur and total salt content of the crude oil.

The distribution of sulphur in crude oil is about linear with respect to boiling-point. This is particularly true of California crude oils [13, 1941]. Thus the sulphur content of the fraction which boils at half-way in the boiling-range (not 50% boiling-point) will be about the same as the sulphur content of the crude oil. The same authors find that the ratio of sulphur in California cracked residuum to the sulphur in the cracked naphtha is about 1:8. Stated in reverse, the naphtha will contain about 55·5% as much sulphur as the residuum.

The salt carried into the plant in the brine associated with the crude oil is a major cause of plugging of exchangers and coking of pipestill tubes. Salt content may be determined by the Universal Oil Products Company's method [34, 1940], Method A-22-40. The following tabulation indicates the theoretical amount of pure salt that could be deposited from 10,000 bbl. per day of crude oil:

Salt content lb./1,000 bbl.	*Salt deposit cu.ft./day*
1,000	29·0
100	3·0
20	0·6

Salt or brine settlers are installed to reduce the salt content as much as possible, but most refiners find difficulty in reducing the salt content to less than $\frac{1}{10}$th of that which is present in the crude oil. A crude oil that contains 20 lb. of salt per 1,000 bbl. as it enters the exchangers requires frequent washouts with water to remove salt deposits in the exchangers and pipestill.

Engineering Design and Operating Data

In order to make material and heat balances over processing equipment it is necessary to determine the specific gravity (or A.P.I. gravity) of fractions covering the entire boiling-range of the crude oil. Such a curve is called the A.P.I. (or gravity) Mid Per Cent. Curve [16, 1941]. Refer to Fig. 3.

The other curves of Fig. 3 are a true boiling-point distillation curve obtained by a fractionating type of distillation [29, 1938] and a flash vaporization curve [16, 1941]

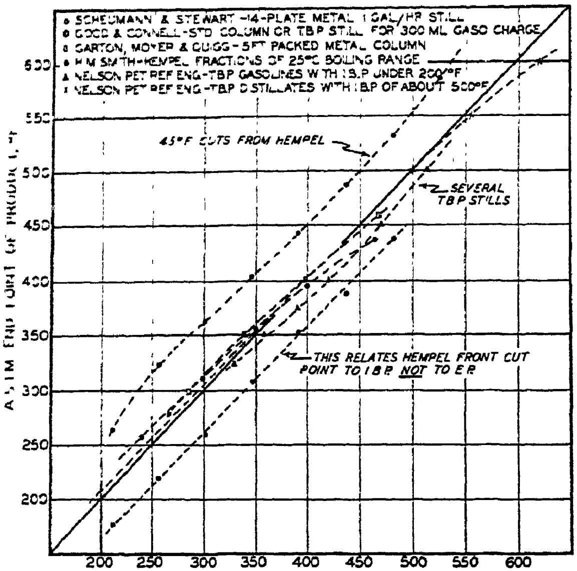


FIG. 2. Relation of A.S.T.M. end-point to true boiling-point cut-point for various distillation equipments. (Courtesy of *Oil and Gas Journal.*)

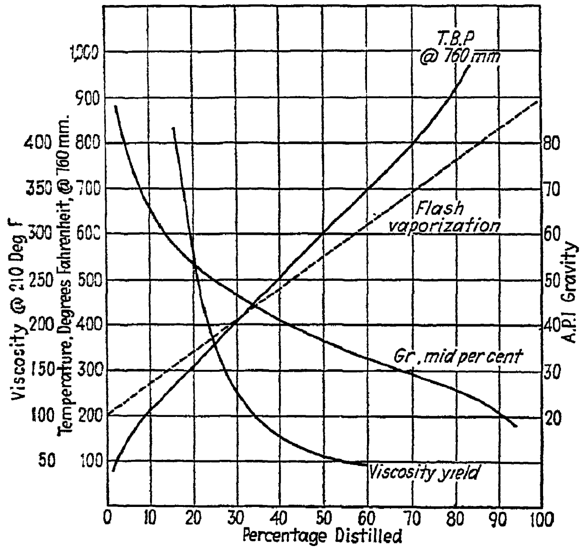


FIG. 3. True boiling-point, flash vaporization, and A.P.I. mid per cent. curves for a 38·6 A.P.I. Mid-Continent petroleum. (Courtesy of McGraw-Hill Book Co.)

obtained by a continuous type of distillation in which the entire oil (liquid and vapour) is kept in intimate physical contact until the vaporizer or separator temperature is attained. The true boiling-point curve is needed in determining yields and the properties of materials in process. The flash curve is necessary in determining the temperatures that must be attained in continuous plant processing equipment, the amount of pressure that can be tolerated, or the amount of steam or vacuum that must be employed. The laboratory equipment and operations for obtaining a flash vaporization curve are elaborate and hence empirical methods of approximating this curve are frequently employed [17, 1941].

Finished distillates are marketed on the basis of the A.S.T.M. (or 10% type) distillation curve and hence a means of converting boiling-ranges of the true boiling-point curve into A.S.T.M. distillation temperatures is necessary. A method of approximating the A.S.T.M. end-point of cuts of known true boiling-point cut-point is shown in Fig. 2 [18, 1944]. Each equipment behaves somewhat differently in this respect and hence Fig. 2 should be used with caution. Preferably the relationships of Fig. 2 should be established experimentally on the particular equipment at hand.

Flash-point is another important but troublesome property which needs to be estimated in the evaluation of solvents or fuel oils. Determinations of the flash-point of products produced in the laboratory mean little because the relationship between laboratory and plant fractionation is seldom known and because steam is used to strip most of the raw products produced in the plant. This difficult situation can be avoided by estimates of flash-point based on the following grossly approximate equation [19, 1944]:

$$F = 0{\cdot}64T - 100$$

in which F is the flash-point ° F. (any kind that is normally applicable to that boiling-range of material) and T is the average boiling-point of the material in the 0–10% distillation-range of the material. Thus, if the 0–10% boiling-range is 250–350° F. (average of 300° F.) flash-points up to 92° F. can be obtained for a well-stripped or fractionated product. Crude oils of high flash-point (30° F. or over) are shipped at reduced railroad freight rates in the United States and meagre data indicate a similar type of equation may be used for estimating the flash-point (Tagliabue closed cup) of crude oils [20, 1945]:

$$F = 0{\cdot}57T - 110$$

in which T is the 0–10% average boiling-point determined in a Hempel-type distillation.

Curves of Properties of Products

Pertinent properties of each product are frequently plotted as so-called Property Curves. Two general types of such curves or data are employed, (1) Mid Per Cent. Curves which show the physical property of small fractions each plotted at the mid percentage point of the fraction, and (2) Cumulative or Yield Curves which show the physical property as a function of the yield of residue (or distillate) materials. The mid per cent. curves can be used to evaluate the yield of a product between any limits of percentage through which the data exists, but the yield curves are useful only with respect to materials which terminate at 100% (Residue Yield Curves) or materials which start at zero per cent. (Distillate Yield Curves). Examples of these two types of curves are given in Figs. 4, 5, and 6 and other examples are given in *Science of Petroleum* by Peters [29, 1938].

Fig. 4 [21, 1945] shows gravity, octane number, and aniline point as mid per cent. curves, and octane number as a distillate yield curve. From these curves the properties of a 10% fraction ranging from 20 to 30% based on crude oil would have the following approximate properties (see Mid Per Cent. Curves):

A.P.I. gravity . . .	48
Octane number . . .	34
Aniline point . . .	135

Fig. 5 [22, 1933] shows residue yield curves of penetration and of float test for a cracking-plant residuum which is being 'worked up' for asphalt. The curves show that a 50% residue from the cracked residuum will have a penetration of about 63, or that an 80% residue or yield will have a float test of about 60. Fig. 6 shows six mid per cent. curves

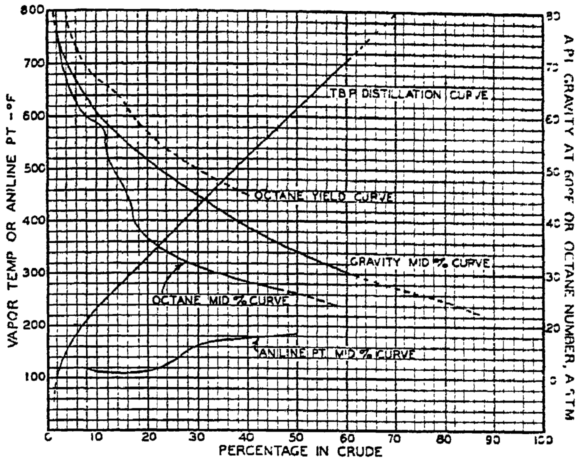


FIG. 4. Evaluation curves of a 37 A.P.I. paraffin intermediate base crude oil. (Courtesy of *Oil and Gas Journal.*)

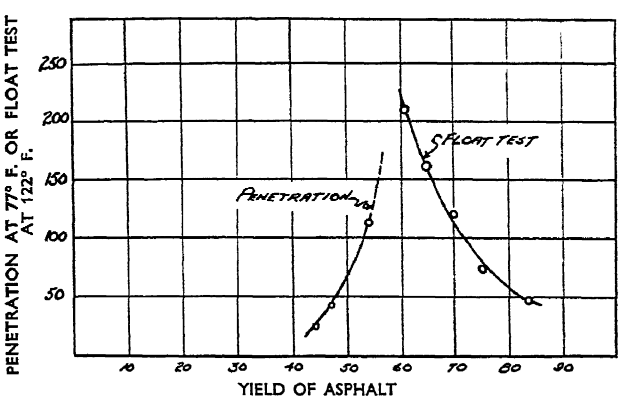


FIG. 5. Penetration and float test yield curves of a cracked residuum. (Courtesy of *Petroleum Engineer.*)

of a distillate fuel oil produced by Houdry catalytic cracking of an intermediate-base chargestock. Nine such analyses are presented by Cauley and Delgass [1, 1946]. Note that vapour temperature is considered (and properly so) as a mid per cent. property. The reverse curvature that is evident in the gravity curve is characteristic of catalytically cracked products and of materials that are blends or mixtures of two stocks.

Another important method of plotting yield and mid per cent. data was introduced by Turner and Canant [33, 1937] and they show charts of the aniline point, gravity, viscosity, final boiling-point of fractions, and octane number of East Texas crude oil. The method involves plotting the physical property of the fraction versus the percentage at which the fraction starts and the percentage at which it ends, and constructing lines of constant value of the property. This is indicated in Fig. 7 [23, 1943], which shows the octane number and Reid vapour pressure of the gasolines that can be made from one Mid-Continent raw gasoline. The use of Fig. 7 is illustrated by the three circle-points which represent:

Percentage of product	*Percentage range based on raw gasoline*	*A.S.T.M. Oct. no.*	*Reid v.p.*
5	15–20	65·0	3·0
25	5–30	65·5	6·4
5	40–45	60·0	1·6

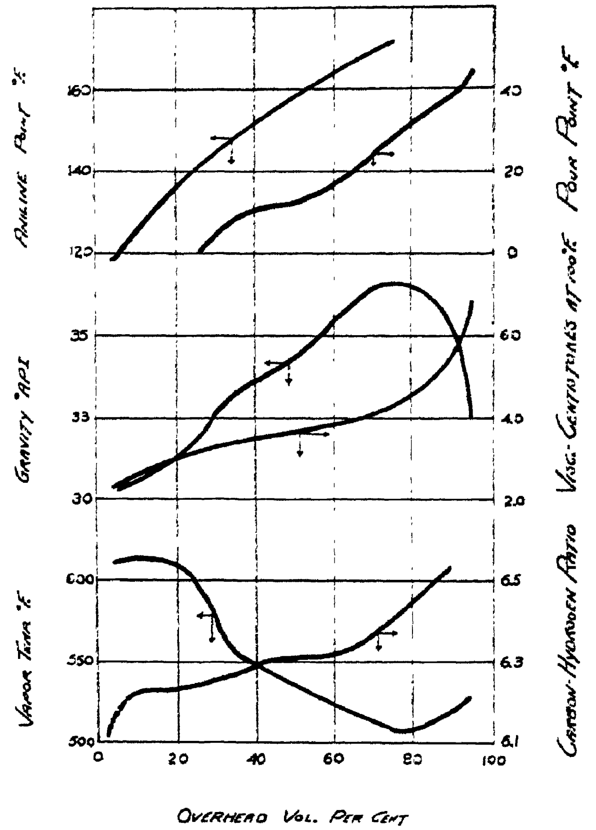


FIG. 6. Six mid per cent. curves on a catalytically cracked distillate fuel oil. (Courtesy of *Oil and Gas Journal.*)

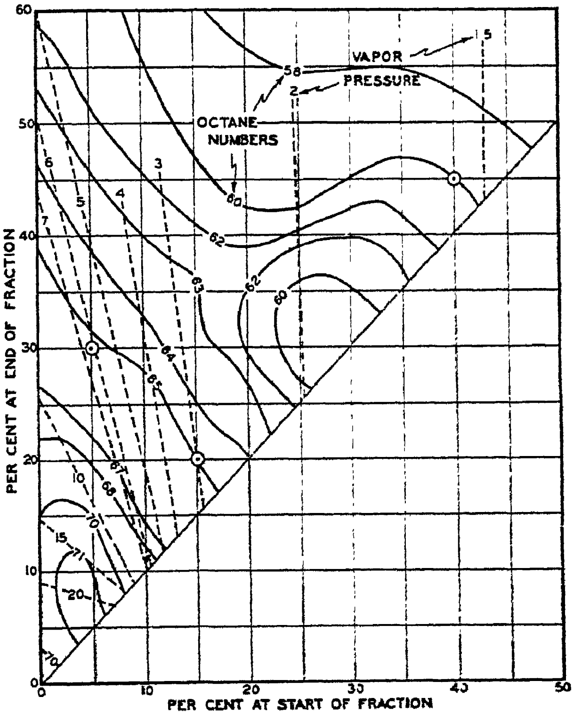


FIG. 7. Octane number and vapour pressure analysis of a Mid-Continent naphtha for aviation gasoline. (Courtesy of *Oil and Gas Journal.*)

The analysis shown in Fig. 1 was used during World War II by a small refiner in producing straight-run aviation gasolines. The octane numbers of the gasolines shown in Fig. 1 are increased by about 23·3-octane number units by the addition of 4 c.c. of tetraethyl lead per gallon.

Major Properties of Products

There is no end to the properties that may at times be significant, but in a general way the most important properties of common plant products are as follows. Note that the properties listed here are primarily those that are needed in evaluating yields and only indirectly are they related to the performance of the products when used.

Aviation Gasoline, Straight Run. Reid vapour pressure, octane number, lead susceptibility, and per cent. sulphur are major properties. Aniline point gives some indication of aromaticity in lieu of octane number data. The end-point and 90% distillation temperatures can be estimated from Fig. 2.

Motor Gasoline. End-point and octane number are important. In a most general way the shape of the A.S.T.M. distillation curve can be estimated from Fig. 8 [6, 1939].

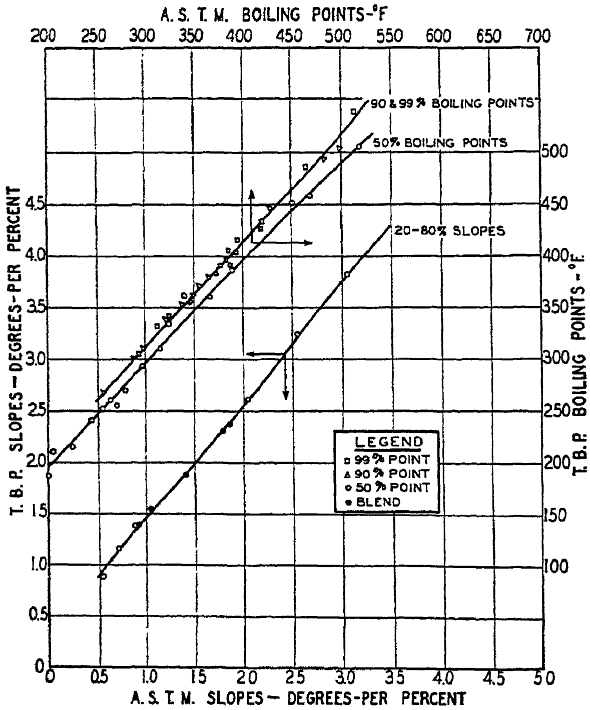


FIG. 8. Relation of slopes and boiling-points of T.B.P. and A.S.T.M. distillation curves.

The lead susceptibility of average gasolines is somewhat as follows [26, 1945].

Clear A.S.T.M. Oct. no.	*Oct. no. with 3 c.c. T.E.L. per U.S. gallon*		
	Straight run		
	0·1% S & lower	*0·1–0·3% S*	*Cracked*
40	62·9	..	..
50	67·9	65·4	..
55	73·6	69·2	70·3
60	77·4	73·0	74·0
65	81·2	77·0	76·5
70	85·1	81·0	78·3

Solvents. Mid per cent. curves of aniline point, per cent. sulphur, and colour are of primary significance in determining the solvency and stability of a petroleum naphtha. Flash-point can be estimated by the equation given above. Crude oils differ widely in the odour of the naphthas produced from them.

Kerosine. Smoke-point, flash-point, and gravity are important. Flash-point is somewhat dependent on the entire boiling-range of the material as well as the lowest-boiling portion, and hence Fig. 9 [24, 1943] is more accurate than the flash-point equation given here. Fig. 9 shows flash-point as a function of the approximate yield of kerosine and the true boiling cut-point of the gasoline (or next lower-boiling product).

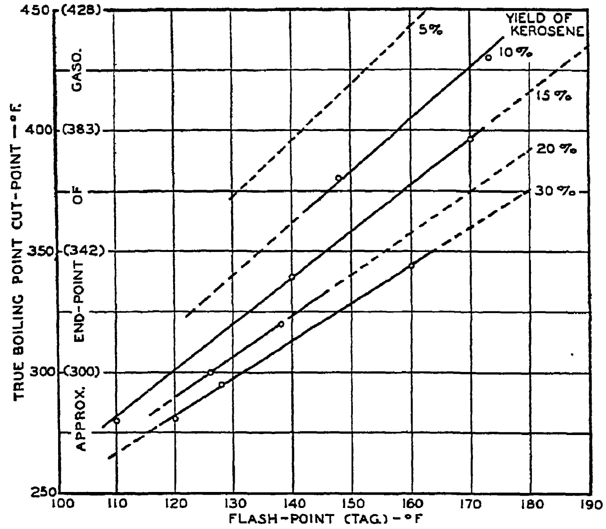


FIG. 9. Approximate relationship of the flash-point of kerosine to the yield of kerosine and the T.B.P. cut-point of gasoline. (Courtesy of *Oil and Gas Journal.*)

Range Oil. Kerosine-like distillates that tend to smoke can be disposed of as range oil or incorporated into tractor-fuel oils.

Diesel Fuel. Pour-point, aniline point or Diesel index, viscosity, and carbon residue are primary considerations. Fig. 10 is an approximate chart of the relation of cetane number, gravity, viscosity, and mid boiling-point of fuels from United States crude oils [25, 1945].

Distillate Fuel Oils. Flash-point, general boiling-range, and aniline point (or Diesel index) are important. Diesel index is more directly related to the tendency to deposit coke or soot than other physical properties.

Cracking Stocks. The carbon residue, colour, aniline point, and tar number [32, 1931] are significant. Some refiners keep the tar number of their cracking-plant recirculation (distilled charge) to less than 5·0 to avoid coking of the tubes. Catalytic cracking-plant feeds should have a colour lower than 2 N.P.A. and should not contain material that boils above about 900° F. The yield of gasoline (400 end-point) by thermal cracking from either gas oil or residual charge stocks is approximately [27, 1936]:

$$\% = 25 + 1{\cdot}5\,(S - T),$$

in which S and T are the A.P.I. gravities of the charge stock and the cracked fuel oil that will be produced.

Mithoff, MacPherson, and Sipos [13, 1941] find that the octane number of thermally cracked gasolines (in plants

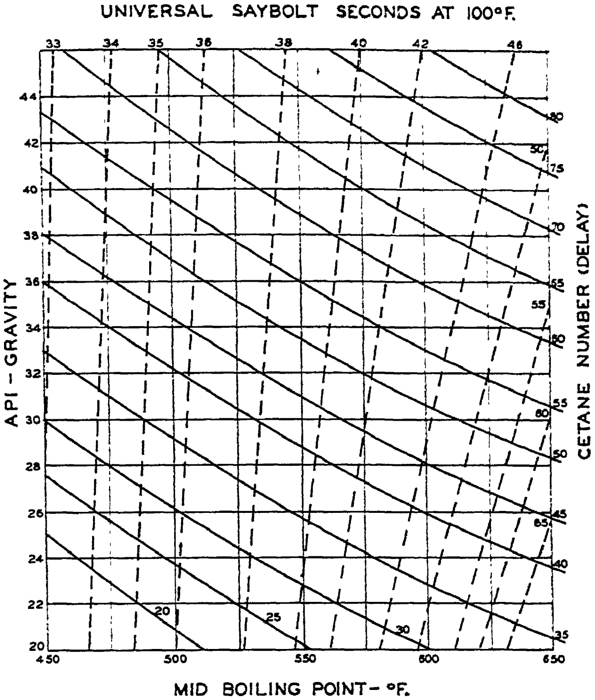


FIG. 10. Approximate relationship of Diesel fuel oil physical properties. (Courtesy of *Oil and Gas Journal.*)

having reaction chambers) is related to the characterization gravity. This they define as the average A.P.I. gravity of the three fractions in the cracking stock which boil at 350°, 450°, and 550° F. at 25-mm. pressure. Most approximately, the relation between characterization gravity and octane number for California stocks is:

$$\text{Oct. no.} = 90{\cdot}8 - 0{\cdot}77(\text{A.P.I.}).$$

The same authors show cracked gasoline yield as a function of the viscosity of the cracked residuum. Such a relationship is superior to yields based on the gravity of the residuum, as suggested by Nelson [27, 1936], because the viscosity of the residuum rather than the gravity is the factor that really keeps the operator from raising the yield.

Wax Distillate and Cylinder Stock. If such materials are to be dewaxed by conventional pressing and centrifuging methods (not solvent dewaxing) the cut between the two materials should be made at not higher than 875° F. and preferably 835° F. According to Davis and Campbell [2, 1933] such a cut-point usually results in a pressible wax distillate. Lower cut-points can be tolerated on the cylinder stock and still retain suitable centrifuging properties. At least mid per cent. curves of gravity and viscosity at 100° F. and 210° F., and a yield curve of viscosity at 210° F. are necessary for evaluation purposes. Pour-point is significant if a so-called 'wax-free' crude oil is being considered. Naphthenic oils also exhibit a better solvency power for many additive agents than paraffinic oils. Many black oils are of naphthenic origin because of their inherently low pour-point.

Asphalts. Penetration and ductility are the main property curves. Due to the difficulty encountered in the plant in vaporizing enough material to obtain low penetrations, an experimental flash vaporization curve is advisable.

Residual Fuels. Flash-point and viscosity are important, and curves of per cent. cut-back oil versus viscosity are useful. Such curves are shown in Fig. 11.

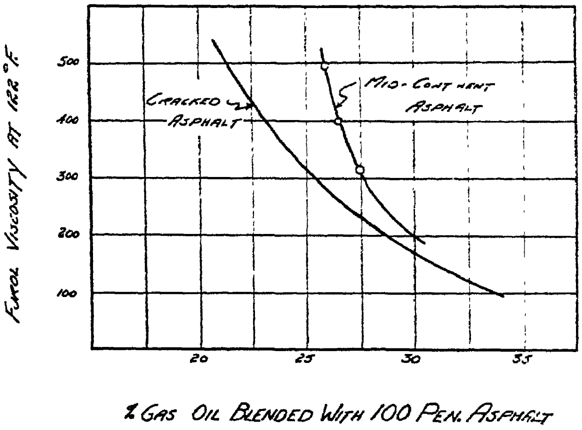


FIG. 11. Cut-back blends for two asphalts. (Courtesy of *Petroleum Engineer.*)

REFERENCES

1. CAULEY and DELGASS. *Oil and Gas J.*, p. 166, 27 July (1946).
2. DAVIS and CAMPBELL. *Oil and Gas J.*, p. 49, 25 May (1933).
3. DAVIS, JONES, and NEILSON. *Oil and Gas J.*, 26 May (1938), also NELSON, W. L., *Oil and Gas J.*, p. 87, 3 Mar. (1945).
4. DOCKSEY, P. *Science of Petroleum*, vol. ii, p. 1091 (Oxford Univ. Press, London, 1938).
5. EGLOFF, G., and NELSON, E. F. *Oil and Gas J.* **35** (7), p. 34 (1936).
6. HANSBURG, M. Masters Thesis, Univ. of Tulsa (1939) or *Oil and Gas J.*, p. 45, 3 Aug. (1939).
7. HEINZE and MARDER. *Brennstoff-Chem.* **16**, 286 (1935).
8. HOUGHTON and ROBB. *Ind. Eng. Chem., Anal. Ed.* **3** (1931).
9. JACKSON, E. A. *Oil and Gas J.*, p. 16, 21 Mar. (1935).
10. KEWLEY, J., and JACKSON, J. S. *J.I.P.T.* **13**, 364 (1927).
11. LANE, E. C., and GARTON, E. L. U.S. Bur. of Mines Repts. of Invest. 3279, Sept. (1935).
12. MINCHIN, S. T. *J.I.P.T.* **17**, 102 (1931).
13. MITHOFF, MACPHERSON, and SIPOS. *Oil and Gas J.*, p. 81, 6 Nov. (1941).
14. NELSON, W. L. *Oil and Gas J.*, p. 91, 2 Dec. (1944).
15. —— *Oil and Gas J.*, p. 107, 16 Dec. (1944).
16. —— *Petroleum Refinery Engineering*, chap. VI (McGraw-Hill Book Co., Inc., 2nd ed., New York, 1941).
17. —— *Petroleum Refinery Engineering*, pp. 241–7 (McGraw-Hill Book Co., Inc., 2nd ed., New York, 1941).
18. —— *Oil and Gas J.*, p. 277, 30 Dec. (1944).
19. —— *Oil and Gas J.*, p. 72, 2 Mar. (1944).
20. —— *Oil and Gas J.*, p. 284, 17 Nov. (1945).
21. —— *Oil and Gas J.*, p. 151, 24 Feb. (1945).
22. —— *Petroleum Engineer*, p. 58, Mar. (1933).
23. —— *Oil and Gas J.*, p. 52, 13 May (1943).
24. —— *Oil and Gas J.*, p. 70, 9 Sept. (1943) and p. 80, 2 Oct. (1943).
25. —— *Oil and Gas J.*, p. 127, 15 Dec. (1945).
26. —— *Oil and Gas J.*, p. 145, 13 Oct. (1945).
27. —— *Petroleum Refinery Engineering* (McGraw-Hill Book Co., Inc., 1st ed., New York, 1936).
28. —— *Oil and Gas J.*, p. 101, 28 Oct. (1944).
29. PETERS, W. A. *Science of Petroleum*, vol. ii, p. 1580 (Oxford Univ. Press, London, 1938).
30. SCHEUMANN, W. W., and STEWART, J. F., A.P.I. Meeting, Tulsa, Okla., 15 May (1935).
31. SMITH, H. M. Tech. Paper 610, U.S. Bureau of Mines (1940).
32. TRUSTY, A. W. *Oil and Gas J.*, p. 22, 8 Oct. (1931).
33. TURNER and CANANT. *Oil and Gas J.*, p. 86, 25 Mar. (1937).
34. Univ. Oil Products Co. Laboratory Test Methods, Chicago, Ill.
35. WATSON and NELSON. *Ind. Eng. Chem.* **25**, 880 (1933).
36. WATSON, NELSON, and MURPHY. *Ind. Eng. Chem.* **27**, 1460 (1935).

ECONOMIC DEVELOPMENTS IN THE PETROLEUM INDUSTRY

By OSCAR TOKAYER

Petroleum Press Service

THE decade since the first four volumes of *Science of Petroleum* were published comprises probably the most momentous years in the annals of the petroleum industry. Not only has it been a period of unparalleled technical advance, greatly stimulated by the exigencies of a global war, but economic developments have also been spectacular, despite the vast amount of physical destruction and the disruption of international trade. Far-reaching changes have taken place in the world's sources of oil supply, while new spheres of demand have been opening up in addition to the ever-broadening field of traditional requirements. Indeed, our whole conception of petroleum as an industrial commodity has altered. It is no longer looked upon merely as a vital source of motive power, of light and heat, or as a raw material for the manufacture of lubricants. Modern science of synthesis has taught us to make use of oil and natural gas hydrocarbons for the production of an almost endless variety of chemicals and other substances, the importance and possibilities of which are as yet unassessable.

While acting as a powerful stimulus in one direction, the war has retarded or thrown back economic progress in others. Highly industrialized belligerent countries, like the U.S.A. and Canada, or even the former neutrals like Sweden and Switzerland, have greatly expanded the productive capacity of their economies, thus creating a large new demand for petroleum products. At the same time many of the raw-material and food-producing countries overseas have been making rapid strides in the establishment of local manufactures, reaching an output often well in excess of local requirements. Again, other countries have benefited from the creation of vast new military bases which involved the building of railways, roads, bridges, ports, aerodromes, workshops, and the like.

The vast amount of shipping required for war, which has led to the unprecedented expansion of shipbuilding in the United States, has added up, despite the heavy losses, to a huge net gain in the world's tonnage. Since the great bulk of the new tonnage is oil driven—the share of the oil-propelled ship in the world's total now amounting to some 74% as against 57% in 1939—demand for bunker oils has risen cumulatively. The world-wide shortage of coal has given a further impetus to the change-over from solid to liquid fuels by many industrial nations as well as in less-developed countries, while the problem of food-supplies and labour shortages has greatly contributed towards the rapid mechanization of farming in many lands. Thus it happened that world consumption of petroleum products to-day has far outstripped its pre-war volume, even though its rapid rate of post-war expansion has, naturally, slowed down since about the middle of 1948.

Growth of Reserves

Such a dynamic advance in consumption would never have been possible without a commensurate increase in the world's established oil reserves, from which the greater supplies could be drawn. On 1 January 1939 the total proved underground reserves of our planet amounted to 34,248 million barrels, according to the most authoritative estimates made at that time. At the pre-war rate of world production of around 2,000 million bbl. annually, these reserves would thus have been adequate, theoretically, for a 17 years' supply. Actually, world production during the period 1939–48 has not been very far off 25,000 million bbl., which means that mankind would have been in a dire situation indeed to-day, were it not for the discovery and development by the oil industry of new vast resources in the meantime.

These new oil discoveries, made primarily in the Middle East, the U.S.A., and Venezuela, have been truly prodigious. Mr. DeGolyer, the well-known expert, puts global reserves, proved and indicated, as at 1 January 1949, at 78,322 million bbl. Thus within 10 years there has been a net gain of over 44,000 million bbl., and if actual output is added, the colossal total of little short of 70,000 million bbl. of new oil has come 'into sight'. The addition of this wealth has been attributable just as much to the finding of new fields as to the extension of reserves (by additional drilling and revaluation) in previously located fields.

Any estimate of reserves is inevitably subject to many uncertainties. It takes neither into account any as yet undiscovered and untested fields, nor does it include new productive formations likely to be found by more intensive search and drilling or the application of new recovery techniques in existing fields. In most instances it takes several years of development before the ultimate potentialities of an oilfield can be assessed at all. Nor is our geological knowledge of the world's oil-producing areas anything like complete or up to date. Despite the wide possible margin of error thus implicit in any such estimate, the following computation (Table I) is, nevertheless, a valuable guide to our understanding of the order of magnitude of reserves of the major oil-producing countries.

The world's known or indicated petroleum resources are thus almost evenly divided between the western and the eastern Hemisphere. The biggest gains in reserves recorded since 1939 took place in the U.S.A., Venezuela, and most of the producing countries of the Middle East. Established reserves in the U.S.S.R., however, are believed to be considerably below the pre-war estimates, although reliable information that could serve as a guide is lacking.

TABLE I

Estimated Proved and Indicated Reserves

(Million barrels)

As at 1 Jan. 1949

Western Hemisphere		
North America		
United States	28,000	
Mexico	850	
Canada	500	
Others	3	
		29,353
South America		
Venezuela	9,000	
Colombia	300	
Argentina	250	
Trinidad	250	
Peru	160	
Others	70	
		10,030
Total Western Hemisphere		39,383

TABLE I (*cont.*)

Eastern Hemisphere		
Africa		
Egypt	120	
Others	2	
		122
Asia		
Middle East		
Bahrein	170	
Iran	7,000	
Iraq	5,000	
Kuwait	10,950	
Qatar	500	
Saudi Arabia	9,000	
Others	1	
		32,621
Far East		
Dutch East Indies	1,000	
British Borneo	150	
Others	242	
		1,392
Europe		
Rumania	350	
Austria	75	
Netherlands	50	
Germany	45	
Others	84	
		604
U.S.S.R.		4,200
Total Eastern Hemisphere		38,939
World Total		78,322

Authority: E. DeGolyer

The only country where the natural oil reserves are made the subject of a regular and exhaustive study is the United States. The statistical evidence thus provided goes to show that domestic reserves, for many years past, did not cease to grow, despite the ever-increasing withdrawals necessitated by actual production. As will be noted from the figures below, new discoveries in the U.S.A. have persistently remained well behind crude-oil output. Thanks, however, to the disclosure of new reserves by the progressive development of existing fields and revisions of previous estimates, the oil industry has succeeded thus far in enlarging its proved reserves. This achievement has only been possible thanks to a far greater exploration and drilling effort.

As the statistics reveal, the rate of new discoveries is wholly inadequate, despite the intensified search which is reflected in the steep rise of wild-cat drilling. This indicates that because wide areas of the U.S.A. have already been drilled up and exploration has to be extended to less promising areas, immense exertions must be made to replace the oil withdrawn from underground, and thus to keep pace with increasing requirements.

The Uptrend in Production

Owing to the big expansion in its proved reserves, the oil industry has been able greatly to expand its production during the past decade and thus meet the world's relentlessly mounting needs. As the following figures show, not even the end of hostilities in 1945 had any visible effect upon the upward trend of production, because the contraction in military needs was more than offset by civilian demands.

TABLE III

World Crude Oil Production

(*In thousand metric tons*)

1938	272,033
1939	284,398
1940	292,800
1941	300,336
1942	276,357
1943	295,274
1944	334,597
1945	353,928
1946	377,094
1947	414,076
1948	471,760*

* Provisional.

The expansion in world output since 1938 has thus been remarkable indeed. As for many years past, the U.S.A. has been its principal factor, contributing to the net gain up to 1948 of some 200,000,000 tons no less than 115,000,000 tons or 58%, and easily maintaining its position as the world's foremost producing country.

The second place among producers is now firmly held by Venezuela, whose vast known resources have been developed in recent years at an accelerated pace. Its output of nearly 70,000,000 tons in 1948 was double the figure for 1939 and now represents about 15% of the world's total. This expansion is the more remarkable because of the severe restrictions which, owing to war-time difficulties,

TABLE II

U.S. Drilling Activity and Petroleum Reserves

	Wells drilled							
	Total	*Wild-cats only*	*Oil-wells producing**	*New discoveries*	*Extensions and revisions*	*Total new oil discovered*	*Production during year*	*Estimated proved reserves**
				(*Million barrels*)				
1938	26,712	2,638	369,640	810	2,244	3,054	1,213	17,348
1939	25,987	2,589	380,390	341	2,058	2,399	1,264	18,483
1940	28,124	3,038	389,010	286	1,607	1,893	1,352	19,025
1941	29,070	3,264	399,960	430	1,539	1,969	1,404	19,589
1942	18,151	3,045	404,840	260	1,619	1,879	1,385	20,083
1943	17,884	3,491	407,170	282	1,202	1,484	1,503	20,064
1944	23,106	3,620	412,220	511	1,556	2,067	1,678	20,453
1945	24,571	4,250	418,000	420	1,665	2,085	1,711	20,827
1946	29,228	4,518	424,000	244	2,414	2,658	1,726	20,874
1947	33,128	5,461	†	445	2,019	2,658	1,850	21,488
1948	39,778	6,877	†	396	3,399	3,795	2,003	23,280

* As at end of year. † Not available.

Authority: U.S. Bureau of Mines; American Petroleum Institute; U.S. Petroleum Administration for War.

Note. Because of a different basis of computation, the above reserves estimates as at the end of 1948 do not agree with those previously given by Mr. E. DeGolyer.

had for some time to be imposed upon the oil industry's operations in Venezuela.

By contrast, oil production in the U.S.S.R., following a fairly steady rise in peace-time, experienced a very severe set-back during the war. Having ranked second in the list with an output of 31,000,000 tons in 1940, the country's petroleum industry was hard hit by the heavy damage inflicted by the Germans upon some of the major Caucasian oilfields. No less serious were the consequences of an acute shortage of materials, equipment, and skilled labour in the principal producing centre of Baku and elsewhere. Since the end of hostilities a sustained recovery has been reported, but by 1948 crude-oil output was still somewhat below the peak reached before Russia's entry into the conflict.

Iran, which is notable for its great potential oil wealth, has also witnessed a swift advance of its petroleum industry during the past decade. After a temporary relapse due to war-time handicaps, output has gone up from 10,359,000 tons in 1938 to as much as 25,000,000 tons in 1948, an increase of 140%. The prominence thus gained by the Middle East as a world centre of oil production has been further enhanced by the meteoric rise of Saudi Arabia and Kuwait. Their great potentialities, unknown ten years ago, have enabled those barren countries to forge ahead as oil producers. After entering the ranks of producing countries for the first time in 1938, the output of Saudi Arabia last year exceeded 19,000,000 tons, while that of Kuwait, only 2½ years after the country entered the ranks of commercial oil producers in 1946, reached 6,700,000 tons.

These six countries together—i.e. U.S.A., Venezuela, Russia, Iran, Saudi Arabia, and Kuwait—accounted for no less than 90% of 1948 world production, as will be gathered from the following table:

In assessing the economic importance of the production of individual countries, due consideration has naturally to be given to the factors—physical, technical, geographical, and other—bearing upon the development of their petroleum resources. Thus Iraq may be cited as a striking example of a country which, with its great oil wealth, might by now have been higher up in the rank of producers had not the development of its oilfields been retarded by the capacity limitations of the existing double pipeline to the Mediterranean. Apart from the curtailment of operations necessitated for some time during the war, production has been maintained almost throughout the past 10 years at a level of over 4,000,000 tons annually. During 1948 the closing of the Haifa refinery necessitated a renewed cut in Iraq production.

The small island of Bahrein, in the Persian Gulf, which is rather more limited by its potentialities, has for some time yielded a stationary crude-oil supply of around 1,000,000 tons a year, which has increased somewhat more recently. Commercial production, established on the Qatar Peninsula, in the Persian Gulf, just before the outbreak of the war, has not yet started. With the huge pipeline projects now in hand, by the completion of which new outlets will be opened for the prolific oilfields of Iran, Saudi Arabia, Iraq, and Kuwait, the Middle East will become one of the world's most important oil-producing and shipping areas.

The once-flourishing oil industry of the East Indies temporarily has fallen a victim to Japanese aggression. In consequence, production which in 1938 had amounted to 7,394,000 tons and approximated an annual rate of 8,000,000 tons before Pearl Harbour dropped to no more than a fraction of its former level. There has, however, been a sharp recovery during the past few years and by

TABLE IV

World Crude-oil Production[1]

(In thousand metric tons)

	1948[2]	*1947*	*1946*	*1945*	*1944*	*1943*	*1942*	*1941*	*1940*	*1939*	*1938*
United States	277,190	250,791	234,215	231,544	226,693	203,138	187,202	189,729	182,657	170,822	164,066
Venezuela	69,700	63,562	56,700	46,368	36,799	25,628	21,141	32,589	26,592	29,344	26,890
U.S.S.R.[3]	30,500[4]	27,000[4]	23,500	20,400	18,000[4]	20,000[4]	25,000[4]	29,000[4]	31,000	30,500	29,700
Iran	25,268	20,418	19,497	17,109	13,487	9,861	9,550	6,711	8,765	9,737	10,359
Saudi Arabia	19,260	12,300	8,200	2,872	1,063	650	620	590	700	539	67
Mexico	8,400	8,052	7,040	6,057	5,500	5,110	5,017	6,430	6,450	6,282	5,460
Kuwait	6,400	2,200	800	..	..	..	..	..	..	..	..
Rumania	4,500	3,810	4,193	4,640	3,525	5,273	5,665	5,453	5,810	6,240	6,610
Indonesia	4,200	1,120	300	1,359[5]	4,400[4]	2,500[4]	1,150[4]	7,950	7,933	7,943	7,394
Argentina	3,300	3,113	2,976	3,266	3,451	3,537	3,377	3,136	2,936	2,651	2,443
Colombia	3,200	3,527	3,189	3,252	3,205	1,911	1,512	3,500	3,634	3,433	3,127
Iraq	3,153	4,478	4,700	4,712	4,271	3,633	2,637	1,568	2,567	4,018	4,364
Trinidad	2,885	2,911	2,890	3,079	3,050	2,950	3,080	2,800	3,075	2,730	2,450
British Borneo	2,870	1,826	300[4]	445[5]	600[4]	500[4]	240[4]	670	955	973	864
Egypt	1,880	1,332	1,280	1,344	1,344	1,258	1,144	1,190	911	959	223
Peru	1,850	1,692	1,663	1,836	1,910	1,949	1,814	1,580	1,605	1,788	2,096
Canada	1,629	983	980	1,093	1,294	1,299	1,333	1,265	1,082	972	864
Bahrein	1,500	1,300	1,100	980	874	923	879	953	993	1,063	1,137
Austria	1,000[6]	940[6]	846[6]	445[6]	1,210[6]	1,100[6]	870[6]	635[6]	413[6]	145[6]	57
Germany	635	577	642	530	710[6]	715[6]	750[6]	900[6]	1,050[6]	745	552
Netherlands	496	213	63	6	2	..	..	..	..	..	..
Hungary	470	570	685	654	810	838	665	422	250	142	37
Ecuador	360	311	307	346	310	305	300	205	310	305	309
India	300	300	284[6,7]	360[6,7]	370[6]	370[6]	350[6]	320[6]	310	320	350
Japan	160	181	190	220[4]	380[4]	400[4]	390[4]	390[4]	375[4]	380[4]	356
Poland	140	128	117	110[4]	350[4]	295[4]	378[4]	425[4]	450	511	507
Burma	[7]	[7]	[7]	[7]	250[4]	150[4]	400[4]	1,051	1,108	1,107	1,059
Other countries	514[8]	441[8]	437[8]	901[8]	839[8]	981[8]	893[8]	874[8]	869[8]	749[8]	692[8]
Total	471,760	414,076	377,094	353,928	334,697	295,274	276,357	300,336	292,800	284,398	272,033

[1] Excluding natural gasoline.

[2] Provisional.

[3] Estimated figures comprising from 1946 onwards production in Sakhalin. For previous years output in Sakhalin is included under 'other countries'.

[4] Estimated.

[5] Including estimated enemy production prior to liberation.

[6] Approximate figure.

[7] The output from Burma and (in 1947–8) of Pakistan is included in the figure for India.

[8] Including U.K., France, Italy, Czechoslovakia, Albania, Yugoslavia, China, Bolivia, Brazil, Morocco, and, until 1945, Sakhalin.

1948 output had regained an annual rate of 4,200,000 tons.

Oil production in Rumania reached its culminating point of over 8,700,000 tons in 1936, since when there has been an almost uninterrupted decline to less than half that figure in 1946. Once fifth among producers, the country has been relegated to a comparatively subordinate position to-day. After the war the Soviet Union has established for itself a dominating position in the Rumanian petroleum industry which is marked by the expulsion and expropriation of all other foreign oil companies. Owing to Russian support a recovery in Rumanian output is reported to have taken place in 1948.

In the western hemisphere, apart from the U.S.A. and Venezuela, no major oil discovery of consequence has been made during the past decade.

In Mexico a relapse in production from 6,750,000 tons in 1937 by well over a million tons followed upon expropriation in March 1938. The subsequent gradual recovery was mainly due to growing supplies from the Poza Rica field, which was found and developed previous to the confiscation. During the war, shortages of materials, in addition to bureaucratic sluggishness, caused a fresh decline, but since the end of hostilities there has been a progressive improvement. Thanks mainly to American assistance, new drilling and producing equipment has been acquired, while refinery and transport facilities have to some extent been modernized and extended.

Rather disappointing so far has been the development of Colombia's production, to which high hopes had once been attached. This applies in particular to the noted Barco concession, covering a wide area in the eastern parts of the country, the productivity of which failed to come up to expectations. At around 3,200,000 tons, crude-oil production in 1948, due partly to prolonged strikes, was only about the same as 10 years ago.

Until 1943 Argentina experienced a slow but steady advance in her production, when it reached its peak of over 3,500,000 tons. Afterwards the difficulty of obtaining adequate supplies of materials and equipment prevented the search for new reserves and production drilling from reaching an adequate level and an inevitable decline ensued. By 1948 output had recovered to 3,300,000 tons after having dropped below the 3,000,000 mark two years previously.

The petroleum industry of Trinidad has, broadly speaking, developed along similar lines. Only by exploiting the existing fields at uneconomically high rates was it possible to maintain output at around an annual figure of 3,000,000 tons throughout the war years. More recently, well yields have shown a gradual decline, despite intensified drilling.

A picture of prolonged stagnancy is presented by the oil industry of Peru. From over 2,500,000 tons in 1936 output dropped to only some 1,600,000 in 1946, but during 1948 a noticeable improvement has taken place, thanks to new discoveries.

Much the same is true of developments in neighbouring Ecuador, which follows Peru at a distance and closes the list of Latin America's more notable oil-producing countries. Since no new discovery has been made for a long time, output has been fluctuating between 300,000 and 350,000 tons annually.

Among the lesser producing countries of the vast continent of South America mention may finally be made of Bolivia, Brazil, and Chile, in none of which the oil industry has thus far outgrown its purely local significance.

Before turning our eyes from the western hemisphere to other parts of the world, brief reference must be made to Canada, which, although of no importance as a supplier to other countries, is one of the major oil producers of the British Empire. A discovery made in the Turner Valley field of Alberta in 1937 led to a swift rise in the country's old-established but small production. Against less than 200,000 tons in 1936, output exceeded five times the figure by 1940, to reach a peak of 1,300,000 tons in 1942. Subsequently there has been a steady decline, until, during the past two years, promising new discoveries have again turned the tide. In 1948 a new record production of 1,500,000 tons was secured and hopes are well justified for a greater increase in future.

The long-established oil production of Burma, amounting before the war to around 1,000,000 tons a year, has been almost completely wiped out, mainly due to deliberate Allied destruction of oilfield and other installations. Owing to the vast amount of reconstruction work that has to be done, and to internal disturbances, recovery is very slow. A more rapid revival has, however, taken place in British Borneo and Sarawak. The oilfields there, the yield of which together was also approaching the 1,000,000-ton mark before Pearl Harbour, have not only quickly regained, but far surpassed, their former level, as soon as development work got into its stride. British Borneo in particular has proved to be capable of further great expansion, reaching in 1948 an output similar to that of Trinidad and having since gained the leading place among the oil producers of the British Commonwealth.

Among Far Eastern producers the oilfields of northern Sakhalin have gained some significance. Though the Japanese failed to raise output in their sector to any major extent, the Russians, who are now in sole control of the oil resources of the island, claim to have made more handsome progress in the fields operated by them.

Hardly more successful have the Japanese been in the development either of their modest established domestic petroleum reserves or of those which they had within their domain in the island of Formosa (Taiwan). Their output from these sources during the past decade rarely exceeded 400,000 tons a year.

Under the stress of war needs, China has also become an oil producer worth recording. A number of wells drilled by the Chungking Government in the Kansu province have been giving rising yields, but although the reserves found hold out some promise for the future, actual development has, for obvious reasons, been rather slow.

The comparatively meagre known petroleum reserves of the sub-continent of India have undergone only minor fluctuations during the war. After a modest rise the yield of around 350,000 tons annually has remained stationary, the diminishing yields from older fields having to some extent been offset by new discoveries. Following the separation of India and Pakistan, the greater part of production has fallen to the new Dominion of India.

Africa's only oilfields of importance are in Egypt, and even this country may be considered as belonging economically and politically to the Middle East. Thanks to a new discovery shortly before the war, Egypt, formerly a small producer, gained considerably in importance as a source of Allied oil supplies during hostilities. From a little over 200,000 tons in 1936 output had risen to about 1,350,000 tons by 1944, not, however, without exposing the productive capacity of the new field to a heavy strain. Thanks, however, to new discoveries in the Sinai Peninsula, a new high production level was reached in 1948 and a further rise in the future is indicated.

In Europe, oil developments have naturally been affected in many ways during the past 10 years. The decline of Rumanian output has, to some extent, been offset by the emergence of Austria and Hungary as oil-producing countries. In the former, oil had been found in commercial quantities in 1936, and the latter followed a year later. Stimulated by Germany's pressing war-time needs, production in Austria went ahead rapidly, attaining a total of over 1,200,000 tons in 1944. Similarly rapid has been the progress in Hungary, where well yields in 1943 reached a high level of 840,000 tons, which could not, however, be fully maintained later on. Neither Austria nor Hungary have thus far been able to concentrate upon an orderly development of their oil industry. Much to the detriment of the economy of these countries, the exploitation of their petroleum resources, both under German and Russian domination, has been carried on without regard to principles of either rational or efficient methods of operation.

In Germany the pressure of war-time needs, of course, also led to a ruthless exploitation of existing fields. From 552,000 tons in 1938 production had risen steadily until the outbreak of war, when all the formerly developed underground reserves began to be drawn upon heavily. By 1941 over 1,000,000 tons of crude were produced, but this pace could not be kept up for long; a decline followed when the fighting ceased and production temporarily dropped below an annual rate of 500,000 tons. A recovery has since taken place under the auspices of the British occupation authorities to 635,000 tons in 1948.

More recently the Netherlands have appeared on the scene as a major European oil producer. Following discoveries made early during the war years, but hidden from the Germans, commercial production was started in 1945, rising until 1948 to nearly 500,000 tons annually, thus placing the country fourth among the continent's producers after Rumania, Austria, and Germany.

As a result of the war, Poland has been eliminated from the rank of oil countries as a major producer. Although her output in the inter-war years was declining continuously, she still produced over half a million tons of crude in 1938. Under German occupation of her oilfields the position did not improve, despite considerable efforts, and the outcome of the conflict has meant for Poland the loss to Russia of her principal fields in eastern Galicia. The smaller fields of western Galicia still left to her did not yield more than 130,000 tons in 1948.

Among the lesser producing countries of Europe there is Albania, whose oil deposits were opened up before the war by the Italians, in the course of the fascist drive for self-sufficiency. Output at times was reported to have approached 200,000 tons annually, but it had dropped below this figure even before Italy's surrender, and there are no indications to show that this figure has ever again been attained.

In Great Britain, oil was found, after a period of prolonged search, shortly before the outbreak of war, but the fields were not large enough and output, though rapidly rising at first, did not exceed 100,000 tons per annum. Since 1943 well yields have been steadily diminishing and by 1948 they had dropped to 44,000 tons annually.

France's small oil output of below 75,000 tons per annum in Alsace did not advance much under German rule, and at the time of liberation even this meagre supply had fallen well below pre-war.

Developments in Oil Refining

Economic trends in world oil refining before the war were determined by many factors. Paramount among them was the steady and universal rise in the demand for petroleum products which necessitated a continuous expansion of available facilities well in advance of actual requirements. Up to 1939 there was always a reserve capacity of refinery plants in existence, large enough to take care of prospective needs as well as of seasonal fluctuations in consumption.

Since the great economic depression of the early thirties, refinery construction received an added impetus from the desire on the part of Governments in some consuming countries to have refineries locally, in contrast to the accepted practice in the industry of erecting refineries near the producing fields or at major shipping centres. By granting preferential treatment to refiners a refining industry was thus created in France with a capacity sufficient to cover domestic requirements from imported crude. In an effort to become 'self-supporting', yet without its own supplies of crude oil, Italy followed the example of France a few years later and similar developments took place in a number of other countries.

Under the impact of war, however, the position changed in various respects. Shortages of materials and skilled labour, together with difficulties of transport, considerably slowed down the expansion of the capacity of existing refining facilities, apart from additions for the manufacture of special products, such as aviation gasoline, required to meet war-time needs. Also many plants were destroyed or severely damaged in the course of the fighting or by a policy of deliberate 'denial'. The ensuing loss in refining capacity (which occurred, of course, in the main in Europe, Russia, and the Far East) was more than offset by new construction, notably in the U.S.A., the Caribbean area, and the Middle East. But since much of the new building was devoted to the provision of special facilities needed to meet exceptional war demands for special products rather than to the extension of basic distillation and refining installations, the net gain in capacity over pre-war was comparatively small in relation to the expansion in crude oil output that had taken place in the meantime.

A compilation of all the available statistical material goes to show that estimated world refining capacity in 1948 amounted to some 9,938,000 bbl. daily, compared with 7,580,000 bbl. in 1939, which is equivalent to an increase of 31%. During the same period the number of plants dropped by 22·5%, from 855 to 662 units. There has thus been a marked extension of refining in bigger plants although, as is obvious from what has just been said, the expansion of world refining capacity has not kept pace with crude-oil production, which increased by almost 70%. The large marginal capacity which existed before the war has consequently been sharply reduced—a fact which more recently has temporarily limited the industry's ability to adjust its supplies to the rapid advance in demand.

The U.S.A. naturally stands out for its huge refining capacity, which has always been the corollary of its predominant place in production. No less than 60% of the world's aggregate capacity in 1948 was concentrated within its borders, where the biggest increase since pre-war has also taken place. A closer study of the statistics reveals that the U.S.A. alone accounted for an addition to refining facilities by over 1,500,000 bbl. daily, a figure equivalent to nearly the net gain in world capacity since 1939. The

American example is also of interest in demonstrating the trend towards increasingly larger units in oil refining. Whilst the number of existing plants declined by nearly 30% between 1939 and 1948, their intake capacity rose at the same time by 50%. The average size of a refinery in the U.S. has thus gone up within 7 years from little over 8,000 to 15,550 bbl. daily.

Urgent war needs also made it imperative to expand refining facilities in the Caribbean area, including the Dutch West Indies, while provisions of the 1943 law led to an extension of existing plants in Venezuela and the erection of new ones, now in the course of construction. Otherwise, few changes occurred in countries of the western hemisphere, apart from a notable expansion in refining capacity in Mexico and limited new construction in Canada.

The rise to prominence of the Middle East as an oil-producing area was naturally accompanied by an expansion of local refining capacity, although the additions failed to keep pace with the growth in crude oil output. By 1948 the available capacity in that area had more than doubled since pre-war.

In Europe new construction since the end of the war has thus far been confined, in the main, to the rebuilding and modernization of refineries damaged or destroyed during the war. Many of the plants were of small size or obsolete and had therefore to be scrapped or they remained shut down permanently. Besides, there has been a concentration of refineries into larger units; as a result, the number of active plants in Europe has declined considerably, while their operating capacity is still below its pre-1939 level. There is, however, a very big expansion of refining facilities in many western European countries under way or contemplated, which is to be carried out partly with Marshall Aid. Although some of these projects may not fully materialize, it is certain that refining capacity in Europe will be substantially extended during the next few years.

Some of the refineries of the U.S.S.R., like those in other countries, suffered much damage. Precise information about them is lacking, but it is reasonable to assume that the rehabilitated refining industry is as yet barely exceeding its pre-war capacity, which had been of the order of 640,000 bbl. daily.

The situation in the Far East, as far as oil refining is concerned, is somewhat similar to that in Europe. A large part of the plant capacity voluntarily destroyed by the Allied 'denial' action or damaged in the course of the fighting has been restored, but both the number of units remaining and their intake capacity still falls considerably short of the corresponding pre-war figures.

The effect of all these developments upon the world's oil refining industry is clearly reflected in Table V.

It is thus mainly in the western hemisphere that refining capacity has increased since 1939, while its advance has been comparatively slow in the eastern hemisphere, a net gain in the former instance by 37%, comparing with one of rather less than 18% in the latter. In absolute terms, however, the increase in the western hemisphere has been nearly six times as great. Since world oil consumption in 1948 was about 60% higher than before the war, it is not surprising that all existing refineries in workable condition and capable of getting the necessary crude were operating at full capacity or even beyond during the past few years. More recently, there has been a marked improvement as new refinery construction has been stepped up, while the pace of growth in consumption has lessened.

TABLE V

Estimated World Oil Refining Capacity

(Thousand barrels daily)

	*1948**		*1939*	
	Number	*Capacity*	*Number*	*Capacity*
Western Hemisphere				
U.S.A. . . .	386	6,002	550	4,456
Caribbean† . .	26	862	19	568
Others . .	71	617	78	437
Total . . .	483	7,481	647	5,461
Eastern Hemisphere				
Europe . . .	120	683	144	720
U.S.S.R. . .	25	650	19	637
Middle East .	8	839	8	409
Far East . .	21	258	32	328
Others . .	5	57	5	25
Total . . .	179	2,487	208	2,119
Grand Total .	662	9,468	855	7,580

* Authority: *Oil and Gas Journal.*
† Including Trinidad and Cuba.

Demand and Supply

The continuous growth of oil demand in the inter-war years, which was only temporarily interrupted by the great depression, was due to two principal sets of causes. One was the progressive industrialization and mechanization of many countries; the other the specific advantages—technical, economic, social, and individual—inherent in the use of liquid fuels compared with other forms of motive power. Petroleum products provide, at relatively low cost, a higher concentration of energy, greater efficiency and speed, better adaptability, more flexibility and convenience. Hence the rapid progress of the motor vehicle, of the oil-burning ship and locomotive, the tractor, the aeroplane, and the Diesel engine in all its diverse applications, not to speak of space-heating and the many industrial purposes for which oil can be used, if not exclusively, at least with greater benefit.

The outbreak of war violently changed the situation. While creating unprecedented new demands by vast military forces engaged in a world upheaval, non-essential requirements had, in most countries, to be reduced to a minimum.

The return of peace, far from causing, as had been anticipated, a serious slump in world oil demand, marked the beginning of an era of renewed vigorous expansion.

Despite the sharp decline in military needs, world oil consumption in 1948 thus already far surpassed that of 1939 and the pace of increase has been steadily accelerating. Characteristic of developments during the war years is the progress of oil-burning in ocean shipping. Whereas in July 1939, out of a total world mercantile tonnage (excluding vessels of 100 tons or less) of 68·2 million gross tons, 54% were running on liquid fuel (in motor ships and oil-fuelled steamers), this percentage had, by June 1948, risen to 76·7% of the fleet which, despite war-time losses, had meanwhile grown to over 80 million gross tons.

Meanwhile, the number of motor vehicles in use throughout the world, which before the war reached a total of some 46 million units, went up to over 52 million until the end of 1947, after having sustained a sharp setback during the intervening years. In many countries the number of motor vehicles on the roads is, however, still below its pre-war level, although this applies as a rule mainly to private cars, while the fleet of commercial vehicles has almost everywhere increased. In wide areas consumption of motor fuel for non-essential uses is, moreover, restricted owing to currency difficulties. However, with agricultural mechanization almost everywhere ahead of pre-war, and oil taking the place of coal in many sections of industrial activity, it is not surprising to see oil consumption forging ahead powerfully and, for obvious reasons, nowhere else more than in the U.S.A.

United States

The American oil industry succeeded in greatly increasing its war-time output both of crude oil and finished products, but, as the following figures reveal, the return of peace did not materially alter the need for ever-increasing supplies. The contraction in military consumption was soon more than offset by the revival of civilian demands. After gaining increasingly in momentum, the country's oil requirements reached a peak towards the middle of 1948, whence a slow-down in the pace of increase followed.

TABLE VI

U.S. Crude Oil Production and Refinery Output

(*Thousand barrels*)

	Crude oil production	*Crude runs-to-stills*	*Motor fuel*	*Kerosine*	*Lubricants*	*Gas oil and distillate fuels*	*Residual fuel oil*
1938	1,214,355	1,165,015	569,162	64,580	30,826	151,774	294,890
1939	1,264,962	1,237,840	611,043	68,521	35,036	161,746	305,944
1940	1,353,214	1,294,162	616,695	73,882	36,765	183,304	316,221
1941	1,402,228	1,409,192	701,294	72,586	39,539	189,177	342,367
1942	1,386,645	1,334,103	608,900	67,474	38,626	196,714	358,901
1943	1,505,613	1,429,738	608,180	72,270	38,679	211,516	417,306
1944	1,677,753	1,665,684	739,340	78,344	41,106	239,152	461,455
1945	1,713,655	1,719,534	798,194	81,024	41,867	249,224	469,492
1946	1,733,424	1,730,197	776,054	104,385	45,645	287,896	431,364
1947	1,856,987	1,852,246	839,998	110,412	51,765	312,173	447,795
1948	2,106,282	2,030,670	921,902	121,853	51,416	380,639	466,141

Authority: U.S. Bureau of Mines.

The figures call for no further comment. They clearly reflect a tremendous development all round, which was stimulated, of course, by the war, but as intimated previously, was by no means exclusively or even decisively due to it. The U.S.A. is traditionally a large surplus producer of oil, although her exports, while contributing substantially to the world's supplies, have rarely amounted to more than 15% of her internal consumption. During the war, her oil industry, apart from having to meet the requirements of her huge armed forces in addition to those of her high-geared industrial economy, thus had also to satisfy a substantial part of her Allies' needs. To what extent her own demands, both military and civilian, have called for the large-scale expansion of the oil industry's operations is apparent from Table VII, which also shows that the U.S.A. has had to resort increasingly to imports in order to meet requirements.

In relation to the country's own needs, the impact of the assistance rendered to the Allies upon the U.S. oil industry's operations has been less spectacular than is generally believed. Statistics rather prove that the country's exports diminished substantially in the earlier stages of the war, and recovered only in 1943, when the deployment of Allied forces in the main theatres of combat was gaining momentum. Shipments abroad, made since 1941 largely under Lend-Lease and consisting later on in very large measure of high-octane aviation fuels, reached their peak in 1944, to drop sharply after the cessation of hostilities early in September of the following year. Since then U.S. exports, as given in Table VIII, have again been made on a commercial basis, but, as will be seen, they remained in 1948 well below their pre-war level; notably so, under the impact of domestic supply difficulties and the world-wide dollar shortage, which became most acute during the later year.

TABLE VII

U.S.A. Domestic Demand and Imports of Petroleum Products

(*Thousand barrels*)

	Domestic demand					*Imports*	
	Motor fuel	*Kerosine*	*Lubricating oils*	*Distillate fuel oil*	*Residual fuel oil*	*Crude petroleum*	*Finished products*
1938	523,003	56,360	21,233	117,449	291,833	26,412	27,896
1939	555,509	60,503	23,713	134,973	323,488	33,095	25,965
1940	589,490	68,776	24,690	160,851	340,163	42,662	41,089
1941	667,505	69,469	30,255	172,824	383,602	50,606	46,536
1942	589,110	69,767	29,057	185,661	405,697	12,297	23,669
1943	568,238	68,598	31,459	208,110	467,108	13,833	49,579
1944	633,582	71,812	32,365	209,540	510,797	44,805	47,451
1945	696,333	75,573	35,334	226,084	523,423	74,337	39,283
1946	734,833	89,166	34,884	242,965	477,151	86,066	48,967
1947	795,015	102,519	36,481	298,273	518,510	97,532	61,857
1948	871,200	112,165	36,385	340,048	500,759	129,093	58,616

Authority: U.S. Bureau of Mines.

TABLE VIII

U.S. Exports and Total Demand for Petroleum Products

(Thousand barrels)

	Exports						Total demand				
	Crude oil	*Motor fuel*	*Kerosine*	*Lubricating oils*	*Distillate fuel oil*	*Residual fuel oil*	*Motor fuel*	*Kerosine*	*Lubricating oils*	*Distillate fuel oil*	*Residual fuel oil*
1938	77,254	50,109	7,504	9,417	29,641	17,920	573,112	63,864	30,650	147,090	309,753
1939	72,076	44,638	8,241	11,881	32,020	17,455	600,147	68,744	35,594	166,993	340,973
1940	51,496	25,377	3,374	10,461	19,140	16,109	614,867	72,159	35,151	179,991	356,272
1941	33,238	27,083	3,221	9,924	16,925	14,114	694,583	72,690	40,179	189,749	397,716
1942	33,834	35,097	2,576	8,272	21,575	12,095	624,207	72,343	37,329	207,236	417,792
1943	41,342	51,577	4,752	8,863	24,957	14,894	619,815	73,350	40,322	233,067	482,002
1944	34,238	100,639	4,888	8,889	43,491	12,536	734,221	76,700	41,254	253,031	523,333
1945	32,998	88,059	6,180	6,575	33,496	11,669	784,392	81,753	41,909	259,580	535,092
1946	40,750	45,389	8,559	11,058	29,353	9,486	780,222	97,725	45,942	272,318	486,637
1947	46,355	47,449	7,252	14,262	29,877	10,623	842,464	109,771	50,743	328,150	529,133
1948	39,840	37,410	3,535	12,990	21,808	12,539	908,610	115,700	49,375	361,856	513,298

Authority: U.S. Bureau of Mines.

As will be noted from these figures, pre-war U.S. exports of the higher-priced products—gasoline, kerosine, and lubricants—have until 1947 been fairly well maintained, and even in the case of gas-oil and distillate fuels there has only been a comparatively modest decline; only overseas sales of crude oil and residual fuel oil dropped sharply. On the other hand, imports of crude petroleum and heavy oils (of which the great bulk of U.S. arrivals of finished products consist) have gone up even more markedly. These contrasting movements clearly indicate a change in the country's oil-supply position. While retaining her place as an exporter of high-quality products, the U.S.A. has to rely in large measure upon supplementary supplies from foreign countries of fuel oils, notably residuals, as well as heavy crudes, from which these fuels can primarily be derived.

United Kingdom

Dependent almost wholly upon imported supplies, the United Kingdom, in conformity with other countries, experienced a rise in demand for petroleum products during the years preceding the war. The small production of natural crude oil discovered locally just before the outbreak of hostilities, reached temporarily a peak of 100,000 tons per annum, but this was not maintained for long, and by 1948 it had dropped to 44,000 tons. Although making a valuable contribution to domestic needs, this output did not, however, materially alter the country's supply position. Home refining, which in normal times played a part in Britain's oil economy, had to be drastically curtailed during the war, owing to the need for the utmost economy in the use of tanker tonnage. Only in the later stages of the conflict did the manufacture of aviation fuels from imported materials in newly established facilities assume major importance. Until 1945, however, refinery operations fell considerably behind their former level, but a strong revival followed subsequently, as is revealed by the statistics in Table IX.

Rapid mechanization of agriculture resulted in a doubling in kerosine (or vaporizing oil) imports, while there was more than a threefold increase in arrivals of gas oil, due mainly to its expanding use for gas manufacture and to the progress of the automotive Diesel. By 1948, gasoline imports, on the other hand, still governed by strict rationing for non-essential purposes, had still not regained their former level, while crude oil purchases reached twice their pre-war volume. In all other instances, except lubricants, post-war demands greatly exceeded their former scale of requirements (see Table X).

Other European Countries

The fighting had hardly ended when all the countries were demanding urgently needed supplies of liquid fuels and lubricants. The liberated nations, before anything else, had quickly to restore their disrupted transport systems to some working order, and this they could do best, apart from the repair and rehabilitation of their railways, by the maximum possible use of road vehicles and the revival of their internal shipping. The shortage of coal and the need rapidly to develop agricultural production, added to their consumption of liquid fuels.

The effect of these diverse factors upon the course of

TABLE IX

Refining and Distillation of Imported Crude and Process Oils in the U.K.

(Million gallons)

	1938	*1939*	*1940*	*1941*	*1942*	*1943*	*1944*	*1945*	*1946*	*1947*
Motor spirit	85·9	90·8	80·1	45·2	75·2	86·0	136·4	124·0	140·0	92·7
Industrial spirit, S.B.P.s, &c. . . .	8·8	7·2	12·7	12·2	11·0	9·8	11·1	10·1	11·1	10·1
White spirit	16·2	16·4	9·6	5·6	0·6	0·0	0·0	0·8	7·8	8·8
Kerosine	26·3	27·7	16·9	8·2	1·8	1·0	0·7	1·2	10·6	28·5
Gas oil and Diesel oil	152·7	158·6	90·6	62·6	19·6	15·2	21·5	30·4	104·1	95·3
Fuel oil (including fuel oil for refinery use)	105·4	96·2	65·3	23·1	32·9	25·1	31·4	39·9	134·3	187·1
Lubricating oil	36·3	44·1	35·8	27·1	37·0	47·2	52·4	60·4	75·7	84·2
Total, liquid products:	431·6	441·0	311·0	184·0	178·1	184·3	253·5	266·8	483·6	506·7

Table X

U.K. Mineral Oil Imports

(*Thousand gallons*)

	Crude oil	*Gasoline*	*Kerosine*	*Lubricating oils*	*Gas oil*	*Fuel and Diesel oil*	*Other products**	*Total*
1938	567,953	1,456,667	206,362	108,198	157,926	687,346	19,053	3,203,505
1939	541,393	1,374,644	207,984	102,322	181,441	574,507	16,516	2,998,807
1940	375,373	1,081,138	272,555	151,848	204,069	925,982	17,764	3,028,729
1941	234,342	1,407,996	291,575	122,980	262,518	1,115,749	27,144	3,462,304
1942	141,916	1,248,531	235,209	135,953	267,121	727,191	29,777	2,785,698
1943	126,524	1,670,420	330,945	106,068	428,174	1,316,201	18,678	3,997,010
1944	163,934	2,901,744	369,132	139,061	618,016	1,336,894	32,006	5,560,787
1945	228,091	2,120,228	349,995	77,209	489,177	1,011,259	47,454	4,323,413
1946	537,266	1,207,987	404,449	89,078	492,503	1,044,505	30,275	3,806,063
1947	615,847	1,196,556	325,440	85,086	423,366	789,567	23,915	3,459,777
1948	1,174,663	1,193,943	408,399	86,419	476,468	1,303,593	30,196	4,673,681

* Principally white spirit.

Authority: Board of Trade Accounts relating to Trade and Navigation.

Table XI

*Oil Imports of Continental European Countries**

(*Thousand metric tons*)

	Crude oil		*Gasoline*		*Kerosine*		*Lubricants*		*Gas and fuel oils*	
	1948	*1938*	*1948*	*1938*	*1948*	*1938*	*1948*	*1938*	*1948*	*1938*
France	7,491	6,969	242	537	..	11	79	70	499	499
Sweden	575	92	557	546	178	110	61	62	1,886	517
Netherlands	1,191	433	212	243	233	253	66	54	690	722
Italy	1,724	1,474	45	99	17	52	50	44	754	955
Germany	303¶	788	546‡¶	1,357	17‡¶	22	13‡¶	388	676‡¶	2,394§
Belgium–Luxembourg	301‡	308	610‡	295	15‡	8	110‡	60	875‡	85
Denmark	20	11	304	341	47	117	43	31	715	382
Norway	..	37	197	177	33	30	24	13	1,068	337
Switzerland	..	..	240	201	39	20	30	19	486	194
Portugal	205†	..	64†	74	40†	50	15†	11	86†	57
Eire	..	..	196	138	88	67	11	11	210	45
Finland	‖	‖	200	137	44	65	22	14	195	32
Total	11,810	10,112	3,413	4,145	751	805	524	777	7,140	6,219

* Excluding bunkers and supplies to the Allied military authorities. † Jan.–Oct. only. ‡ Approximate figures. § Including residues for further treatment. ‖ Included in figures for gas oil and fuel oils. ¶ Including imports into the Western Zones only.

Authority: Official trade statistics of the various countries; compiled by the Petroleum Press Bureau.

imports in 1948, as compared with pre-war, is clearly shown in Table XI.

U.S.S.R.

Very little official information has been published about the oil-supply position in the Soviet Union. All that can be assumed is that at the beginning of 1949 annual production is still below its pre-war level of 31,000,000 tons. The current Five-Year plan, which came into effect in 1946, envisaged originally for 1950 an output of 35,400,000 tons, and according to subsequent announcements it was expected to realize this aim by 1949.

In addition to petroleum supplies from domestic sources, Russia has at her disposal also the sizeable quantities of petroleum products delivered to her under reparations or trade agreements by Rumania, Hungary, and Austria. Very little oil is being exported from Russia, and there are indications that the country is scarcely able to meet all her fast-growing oil needs from the sources directly at her disposal.

Trend of Oil Prices

Rapid technological progress, increasing operating efficiency, and fierce competition combined to bring about an almost continuous decline in prices for petroleum products in the inter-war years. Nor did the outbreak of hostilities in Europe produce an immediate boom in oil as it did in some other commodities. The market remained comparatively stable both during the months immediately before and after September 1939. A sharp rise in domestic demands and the inauguration of Lend-Lease in the spring of 1941 resulted in a strengthening of the price structure, and when the U.S.A. entered the conflict price ceilings, based on the quotations of 2 October 1941, were introduced for all petroleum products on 1 March 1942.

Up to early 1946 prices remained more or less stable on a level not very different from that existing before September 1939, with the exception of fuel oil, for which, owing to rather acute shortages, considerable increases had to be granted. Eventually, however, the price-control system was abolished from June 1946, and a general upward movement started, in the course of which quotations, as shown in Table XII, were carried far above their former levels, until a partial reaction followed late in 1948 which continued well into 1949.

According to computations of the *Petroleum Press Service* the price index for petroleum products had risen by the middle of 1948 from 100 during the basic period of 1936 to 1938, to 216·1 for crude petroleum, 213·0 for gasoline, 226·8 for kerosine, 283·7 for gas oil, and as much

TABLE XII

U.S. Market Quotations

End of month	*Gasoline* Reg. Grade§*	*Kerosine* 41 43w.w.*	*Gas oil* D.I.48–52*	*Fuel oil† Grade 'C'*	*Crude oil‡ Mid-Cont. 36–36·9°*
Sept. 1938	4·625–4·75	4·00	3·50–3·625	0·60–0·65	1·22
Mar. 1939	4·25	3·625–3·875	3·375–3·625	0·70–0·72	1·02
Aug. 1939	5·25–5·50	3·75–3·875	3·625–3·75	0·78–0·80	1·02
Sept. 1941	6·25–6·625	3·875–4·00	4·00	0·85–0·96	1·17
Mar. 1942	5·50–5·75	3·875–4·375	4·00	0·85	1·17
Jan. 1943	5·50–5·625	3·875	3·875–4·00	0·85	1·17
Apr. 1943	5·625–5·75	4·125	3·875–4·00	0·85–1·27	1·17
Aug. 1944	5·75	4·125	4·00	0·97	1·17
Jan. 1946	5·625	4·625	4·50	0·90–0·97	1·17
June 1946	5·625	4·625	4·50	1·18	1·27
Dec. 1946	6·75–7·00	5·50–5·75	5·125–5·75	1·38–1·59	1·62
June 1947	8·00–8·25	6·75–7·50	5·875–6·00	1·68–2·50	1·87
Dec. 1947	8·50–12·00	9·00–10·25	8·25–10·00	2·46–3·50	2·57
June 1948	8·50–14·50	9·00–11·00	8·25–12·50	2·46–3·60	2·57
Dec. 1948	9·00–12·00	9·00–10·50	7·875–10·00	2·00–2·50	2·57
Mar. 1949	9·00–12·00	9·00–9·75	7·125–8·25	1·35–1·60	2·57

* Prices in cents per American gallon f.o.b. Gulf Coast Bulk Markets. † Dollars per barrel, prices f.o.b. Gulf Markets. ‡ spot prices ex wharf, excl. taxes, in dollars per barrel. § 70–72 octane leaded, since December 1947; 70 octane leaded, since August 1939; earlier, 'U.S. Motor Gasoline'. ‖ 30° grav., transparent, until March 1938 incl.

as 375·6 for fuel oil. Remarkable as these increases were, they represented in the main belated adjustments to greatly altered economic conditions in the petroleum industry; yet, even so, they compare favourably with the general rise in commodity prices in America. In the course of the set-back that followed, crude oil prices, due largely to a sharp curtailment in production, remained unchanged, while gasoline and kerosine were affected only to a minor extent. Heavy oils, especially residual fuels, however, lost much ground owing mainly to the recession in the demand for the latter. On balance, prices in spring 1949 were generally still about twice their pre-war level.

In considering these price changes, account must be taken of the fact that the American crude-oil supply position has fundamentally changed since before the war owing to the gradual exhaustion of many old-established fields and the consequent disappearance of those 'bottled up' supplies which upset the price structure so often in the past. The absence of any unwieldy excess output of crude is further underlined by the effective production controls exercised by the State Governments to ensure the most economic flow of oil from existing fields with the object of keeping production as close as possible to requirements. The cost of exploration and drilling have increased enormously, and so have the cost of refining and distribution. To cope with the world's rising demand, the oil industry had thus to embark upon a vast capital expansion programme, the financing of which is only possible by adequate prices and sales proceeds, as the bulk of this programme must be financed from the industry's own revenue. The need persists for an ever-increasing scale of exploration and drilling.

Oil Industry Finance

Gross investment in U.S. oil operations was estimated some years ago at around $15,000 million (£3,750 million at the current rate of exchange), and in view of its subsequent growth it must now have reached a figure far in excess of this gigantic total.

A wide measure of confirmation of these estimates is provided by the annual statistical survey of oil company finance produced by Messrs. Joseph E. Pogue and F. Coqueron for the Department of Petroleum Economics of the Chase National Bank of New York. The survey combines the finances of a group of thirty American concerns, and is compiled from annual reports and other information supplied by the companies themselves. The gross investment of these companies, which constitute about two-thirds of the domestic oil operations of the U.S.A. and an appreciable part of the international petroleum trade, totalled $14,776 million at the end of 1947, and their net investment was $7,069 million. The difference of $7,707 million between gross and net figures represents reserves for depletion, depreciation, and amortization.

Annual gross expenditures on extensions, improvements, and the acquisition of new assets during the 10 years to 31 December 1947 are set out in the following table, together with the amounts provided each year for depreciation, &c.

TABLE XIII

Gross and Net Investment of 30 U.S. Oil Companies

($ millions)

	Gross expenditure	*Written off or extinguished*	*Net expenditure (gross less amounts extinguished)*
1938 . .	668	516	152
1939 . .	664	515	149
1940 . .	656	534	122
1941 . .	810	538	272
1942 . .	785	542	243
1943 . .	930	608	322
1944 . .	1,094	776	318
1945 . .	1,112	976	136
1946 . .	1,377	763	614
1947 . .	2,076	867	1,209
10-year total	10,172	6,635	3,537

The figures show that over the 10-year period no less than $10,172 million was expended by the thirty companies; that $6,635 million, or 65%, was amortized in one form or another, and that the net increase in assets shown in the companies' books was only $3,537 million, or no more than 35% of outlays. The period covered by the table falls into two main sections—the years up to the end of 1941, when the U.S.A. entered the war, and the war years themselves—1945 being included under the latter heading because a state of active war existed during the greater part of the year, and because the tempo of oil operations could not be slowed down immediately after the cessation of hostilities.

The return on the aggregate invested and borrowed capital of the thirty companies during the past 10 years is tabulated below. It should perhaps be explained that the invested capital shown is something quite different from either the gross or net investments in oil discussed in previous paragraphs. It consists of the aggregate of money actually put into the companies by stockholders or lent to them by outside investors.

TABLE XIV

Profits and Dividends

	Average invested capital	*Net profit*	*Dividends paid**	*Return on invested capital*	
				Net profit	*Dividends*
	(*Million dollars*)			(*per cent.*)	
1938	5,923	300	199	5·1	3·4
1939	5,973	321	188	5·4	3·1
1940	5,997	377	209	6·3	3·5
1941	6,031	530	251	8·8	4·2
1942	6,154	404	221	6·6	3·6
1943	6,351	510	242	8·0	3·8
1944	6,648	639	288	9·6	4·3
1945	6,998	602	291	8·6	4·2
1946	7,428	763	331	10·3	4·5
1947	8,181	1,219	425	14·9	5·2

* On common and preferred stocks.

The moderate rate of profit on invested capital is brought out strongly in the above figures. It will be seen that the highest return in any year was the 14·9% earned in 1947, which, as already noted, was an exceptionally good year for oil undertakings. The average return over the whole period was only 8·3%, which cannot be regarded as a high level of earnings for an industry in which heavy risks have to be taken. Oil company earnings, moreover, are below rather than above those of American industry in general, the figure of 14·9% in 1947, for example, comparing with an average of 17·0% for a large group of general manufacturing concerns.

Apart from the American oil industry, the most important group of oil companies is that financed by British capital. There is a wide difference between the U.S. and British concerns in that the latter, with quite minor exceptions, carry on their producing operations abroad, and also conduct a large proportion of their refining and distributive operations in overseas countries. The three major British companies are the Anglo-Iranian Oil Company, in which the British Government has a majority interest, the Burmah Oil Company, and Shell Transport and Trading Company. Combined issued capital of these three concerns is £101 million and the book value of their assets at the end of 1947 exceeded £200 million.

Their profit-earning capacity was seriously affected by war conditions that did not touch most of the U.S.A. concerns, operating mainly within America. Thus the Royal Dutch-Shell group, in which Shell Transport and Trading has a two-fifths interest, sustained severe losses in the Dutch East Indies and other war areas, while the Burmah Company's oilfields and refineries were completely destroyed in 1942 to prevent their falling into the hands of the Japanese. Earnings of the Anglo-Iranian Company were heavily reduced at one time during the war through a cut in output necessitated by shipping difficulties, but have since recovered to a record level under the combined influence of a great increase in production and higher selling prices. These vicissitudes are reflected in the earnings record of the three companies, combined net profits dropping from £16·7 million in 1938 to £10·2 million in 1943, to recover to £24·8 million in 1947. Dividends were heavily reduced during the war, but have since shown a rising tendency.

It may, indeed, be claimed that, as far as its major components in both America and Britain are concerned, the oil industry, despite its many hazards, is no less sound financially than it is technically efficient.

SECTION 2

CHEMICAL AND PHYSICAL PROPERTIES OF PETROLEUM HYDROCARBONS

Hydrocarbons in Petroleum	A. N. SACHANEN
The Chemistry of Paraffin Hydrocarbons	J. HABESHAW
The Chemistry of Naphthene Hydrocarbons	W. J. OLDHAM
The Chemistry of Aromatic Hydrocarbons	W. J. OLDHAM
The Chemistry of the Olefine and Diolefine Hydrocarbons	F. A. FIDLER
Mechanisms of Organic Reactions	F. C. WHITMORE and N. C. COOK
The Fractionation, Analysis, and Isolation of Hydrocarbons in Petroleum	B. J. MAIR and F. D. ROSSINI
Chemical Thermodynamic Properties of Hydrocarbons	F. D. ROSSINI
High-Pressure Vapour-Liquid Equilibria in Cycling Operations	D. L. KATZ and M. J. RZASA

HYDROCARBONS IN PETROLEUM

By A. N. SACHANEN

Socony-Vacuum Oil Co., Inc., Paulsboro, N.J.

Introduction

THE ultimate goal of petroleum chemistry in its analytical aspects is to resolve petroleum or petroleum products into individual hydrocarbons and other components. This problem, quite feasible for petroleum gases and light liquid products, seems to be hopeless for high-boiling fractions which may contain an innumerable quantity of various entirely unknown hydrocarbons and other constituents. Thus the separation and quantitative determination of different classes of hydrocarbons and other constituents of petroleum is as important as the separation and identification of individual components.

The hydrocarbons of petroleum are conventionally and broadly classified as paraffins, naphthenes, aromatics, and unsaturates. This classification is quite satisfactory for low and medium molecular weight hydrocarbons, in which the presence of an aromatic or naphthenic ring or a double bond imparts characteristic properties of these structures. But the classification becomes ambiguous for high molecular weight hydrocarbons which may contain different structures in one molecule without imparting the characteristic properties of one dominating structure. A high molecular weight hydrocarbon with aromatic and naphthenic rings and long paraffin side chains would possess paraffinic, aromatic, and naphthenic properties to an extent depending upon the proportion of these structures. The ring analysis developed by Waterman and his associates obviated these difficulties in a simple and logical manner. According to this method, the composition of such complex hydrocarbons, as well as of petroleum fractions, is expressed in terms of the percentage of aromatic rings, naphthenic rings, and paraffinic side chains. From this standpoint, ethyltetrahydronaphthalene, for example, would consist of 48 % aromatic rings (C_6H_4), 34 % naphthenic rings (C_4H_7), and 18 % paraffinic side chains (C_2H_5). The description of the ring analysis is beyond the scope of this chapter and can be found elsewhere [43, 1945]. The data expressed in terms of ring analysis are of primary importance for characteristics of high-boiling petroleum products, as well as of crude oils.

The wide application of ring analysis, however, does not eliminate determination of the conventional classes of hydrocarbons in petroleum in so far as it is feasible. Ring analysis has its own shortcomings, both of method and of practice. The refiner or chemical manufacturer is interested more in the content of various hydrocarbons and other constituents than in the content of structural fragments. Thus the application of ring analysis to gasolines does not present any advantage as compared with the total determination of various hydrocarbon classes, which is quite feasible for such products. The hydrocarbon classes present in petroleum may be classified more specifically as follows.

The paraffins represent the well-defined class characterized by the saturated non-cycle chain structure of hydrocarbons. Other structures are absent in these hydrocarbons.

The naphthenes present in petroleum belong to the saturated five- and six-membered ring hydrocarbons. The presence of other rings of naphthenes in petroleum has not been proved at the present time. The naphthenes are monocyclic in low-boiling fractions and polycyclic in high-boiling fractions.

Like the naphthenes, the aromatics in petroleum are both monocyclic (in low-boiling fractions) and polycyclic (in high-boiling fractions). The classes of naphthenes and aromatics are not so sharply defined as paraffins, because of the presence of rather long paraffinic side chains in these hydrocarbons, as well as of combined naphthenic and aromatic rings. Strictly speaking, the class of naphthene-aromatic hydrocarbons should be introduced in the classification. It should be pointed out, however, that even one aromatic ring in a polycyclic hydrocarbon imparts the aromatic properties, e.g. an abnormal specific dispersion, greater solubility in solvents, capacity for sulphonation, &c. Thus the aromatic hydrocarbons present in petroleum may be specified as six-membered cyclic hydrocarbons with resonating double bonds, which have the aromatic properties specified above and associated with the presence of one or more aromatic rings in the molecule.

Unsaturated hydrocarbons, absent in straight-run products, represent an important class of hydrocarbons in cracked and some other synthetic products. By 'unsaturates' is meant all hydrocarbons which have one or more active double bonds in a molecule of any structure, aliphatic or cyclic. The presence of an active double bond imposes its characteristic properties at least on hydrocarbons of low and medium molecular weight, including perhaps those of gas oils. Unsaturates of high molecular weight are almost unknown, and there are no reliable methods of evaluating the content of unsaturates in high-boiling fractions.

Oxygen, sulphur, and nitrogen compounds are beyond the scope of this chapter. The content of such compounds in low- and medium-boiling petroleum fractions is usually very small, and hydrocarbons are by far predominant constituents of these fractions. However, the content of the so-called 'resinous and asphaltic' compounds, which contain oxygen, sulphur, and eventually nitrogen atoms in their molecules, may be very high in heavy crude oils and heavy residues, amounting to 50 % of total.

Methods of Separation and Determination of Hydrocarbons

The physical methods for determining the chemical composition of petroleum are by far the most important and most generally used; they may be divided into two main groups. To the first group belong such methods as fractional distillation, crystallization, solvent treatment, and adsorption (desorption), by which individual hydrocarbons or hydrocarbon fractions are actually separated according to their physical properties: boiling-point, melting-point, solubility, or adsorption characteristics.

To the second group belong other methods in which no actual separation takes place; the determination of hydrocarbons or hydrocarbon classes is calculated on the basis of a certain physical property, which is either a linear function of the composition (specific gravity, refractive index or various functions of both, aniline point, &c.) or is determinable for each constituent independently of the others (infra-red, ultra-violet absorption, Raman effect, mass spectra).

Thus only physical properties which are well known for individual hydrocarbons or hydrocarbon classes can be used for determining the chemical composition of petroleum. Such properties as fluorescence or optical activity are almost useless from this standpoint, since the hydrocarbons causing them are entirely unknown. Viscosity is a property easily determinable for any fraction and is well known for various hydrocarbons, but the viscosity method seems to be of little value for determining the composition of fractions, since there is no linear relationship between the viscosity of mixtures and their composition. All these considerations limit the application of physical methods to the problem in question.

The methods of fractional distillation (under atmospheric pressure, *in vacuo*, azeotropic, &c.), well developed and perfectioned in the last 10–15 years, are the most powerful tool for effective separation of petroleum hydrocarbons. Other physical or chemical methods can be successfully used only in conjunction with fractional distillation.

The use of infra-red and Raman spectra and mass spectrometry gives very promising results for narrow fractions containing a limited number of hydrocarbons. If the narrow fractions consist of hydrocarbons of the same class, e.g. of isomers boiling in a very narrow temperature range, these methods excel all others for purpose of identification and quantitative determination. On the other hand, the application of such methods to large fractions containing a great number of individual hydrocarbons is made practically impossible by the superimposition of absorption bands or lines. Thus the combination of very efficient fractionation with infra-red and Raman spectra and mass spectrometry will contribute much to the knowledge of the chemical constituents of petroleum.

Chemical methods for determining the chemical composition of petroleum may be classified as general methods, for determining the general structure of petroleum hydrocarbons, and as specific methods, for separating the specific classes of hydrocarbons or, less frequently, the individual hydrocarbons. The general methods are based upon the knowledge of the H:C ratio, or various other properties, before and after hydrogenation, in conjunction with the molecular weight. The above-mentioned ring analysis is closely related to these methods. The specific chemical methods are purely chemical; they require specific reagents for separating various classes of hydrocarbons or, eventually, individual hydrocarbons. Such reactions as sulphonation, nitration, hydrogenation, dehydrogenation, halogenation, oxidation, &c., are widely used for separating various hydrocarbons which enter the above reactions selectively as compared with other hydrocarbons not susceptible to those reactions.

As has been mentioned above, the individual hydrocarbons only in few cases can be separated by the chemical methods which usually separate the whole group of hydrocarbons reacting with the reagent used. A combination of the physical and chemical methods, however, gives the best results of separation, since the chemical methods, appropriately applied, simplify the final fractionation of individual hydrocarbons.

Individual hydrocarbons, hydrocarbon classes, and structures identified and determined in petroleum are discussed in the following sections devoted to the conventional broad petroleum fractions and products: gasolines, kerosines, and gas oils, lubricating oils and petroleum wax. Heavy residues and petroleum asphalts, containing a large proportion of non-hydrocarbon constituents, are beyond the scope of this chapter.

Gasolines (Naphthas)

Natural Gasoline. Natural gasoline is manufactured from natural or casing-head gas by compression or, more frequently, by absorption under pressure. The chemical composition of natural gasoline depends upon the composition of natural gas and, to a greater extent, upon the pressure used in the manufacturing process. The vapour pressure of natural gasolines follows very closely the chemical composition: the higher the vapour pressure the richer the gasoline in low molecular weight hydrocarbons—propane and butanes. Table I gives the composition of a high vapour-pressure natural gasoline consisting largely of propane and butanes. Stabilization of natural gasolines separates propane and excess butanes, to produce a stabilized natural gasoline of proper vapour pressure for use in motor fuels. Butane-free natural gasolines may easily be produced if required. Table II contains data on the composition of raw and stabilized natural gasolines.

TABLE I

Composition of 80-pound Natural Gasoline (Texas)

	Mol. %
Methane	None
Ethane	Trace
Propane	38·7
Isobutane	10·0
n-Butane	18·3
Pentanes	20·0
Heavier	13·0

TABLE II

Composition of Raw and Stabilized Natural Gasolines

	Raw	*Stabilized*	*Debutanized*
A.P.I. gravity (60° F.)	92·5	77·8	74·5
Specific gravity (60°/60° F.)	0·631	0·676	0·687
Reid vapour pressure (lb./sq. in. 100° F.)	60	17·5	11·0
Ethane (% by vol.)	1·5	..	..
Propane	14·7	..	..
Isobutane	10·2	1·5	..
n-Butane	30·3	15·3	3·2
Isopentane	4·8	7·2	8·5
n-Pentane	15·0	21·0	24·5
Heavier	23·5	55·0	63·8

While the content of lighter hydrocarbons in natural gasolines depends largely upon the pressure in the manufacturing process, the content of heavier hydrocarbons, pentanes and up, depends upon the composition of natural (casing-head) gas and crude oil associated with the gas. The data on the content of heavier hydrocarbons in a stabilized butane-free Mid-Continent [26, 1946] and California [3, 1942] natural gasolines are given in Tables III and IV. These data show that natural gasolines, even stabilized and butane-free, are predominantly paraffinic, containing 80% or more paraffins. Normal paraffins predominate in a Mid-Continent natural gasoline, while that from California is richer in isoparaffins. Naphthenes, cyclopentane and cyclohexane with their derivatives, represent from 10 to 20% of stabilized natural gasolines; the content of aromatics is small, not exceeding 1–2% of the total gasoline.

The so-called 'condensate' produced from distillate wells has the properties and composition of natural gasoline but contains a much smaller proportion of propane and butanes and a greater proportion of heavier hydrocarbons, hexanes and upwards.

TABLE III

Hydrocarbons in Mid-Continent Butane-free Natural Gasolines

Hydrocarbon	*% by volume*
Neopentane	0
Isopentane	15–30
n-Pentane	20–30
Cyclopentane	0·5–1·5
2, 2-Dimethylbutane	0·3–0·6
2, 3-Dimethylbutane	0·1–0·3
2-Methylpentane	6–9
3-Methylpentane	3–5
n-Hexane	8–10
Methylcyclopentane	2–4
2, 2-Dimethylpentane	0·1–0·3
Benzene	0·2–0·5
2, 4-Dimethylpentane	0·1–0·3
Cyclohexane	2–4
1, 1-Dimethylcyclopentane	0·2–0·5
2, 3-Dimethylpentane	0·2–0·5
2-Methylhexane	3–4
n-Heptane	2–3
Methylcyclohexane	1–2
Heavier	4–7

TABLE IV

Hydrocarbons in California Unstabilized Natural Gasoline

Hydrocarbon	*% by volume*
Methane and ethane	0·5
Propane	7·5
Isobutane	8·5
n-Butane	28·8
Isopentane	11·3
n-Pentane	9·9
Cyclopentane	0·9
Isohexanes	7·5
n-Hexane	3·9
Methylcyclopentane	2·4
Benzene	0·7
Cyclohexane	1·1
Dimethylcyclopentanes	3·0
Isoheptanes	3·2
n-Heptane+isooctanes	1·6
Methylcyclohexane	1·5
Toluene	0·7
n-Octane+heavier	7·0

In contrast to natural gasoline or condensate, absorption gasolines from cracked gases differ by the presence of unsaturated hydrocarbons which may amount to 40% of the total. Tannich, Thomas, and Padgett [49, 1940] fractionated a 'plant-stabilized' naphtha and determined the percentage of unsaturates in the narrow fractions by the iodine-thiocyanate method. The total percentage of unsaturated hydrocarbons in the gasoline is 27·2% and the percentage in the narrow fractions varies from 32·0 to 15% (by volume), decreasing from lighter to heavier fractions.

It should be added that the non-hydrocarbon constituents of natural gasolines, mostly mercaptans, are usually present in insignificant quantities not exceeding a small fraction of 1%.

Straight-Run Gasolines. The chemical composition of straight-run gasolines has been studied more thoroughly and completely than that of other petroleum products and fractions. The problem is simplified by the absence of olefines and other unsaturates; only paraffins, naphthenes, and aromatics are present in straight-run gasolines. Derivatives of cyclopropane, cyclobutane, cycloheptane, &c., have not been found in gasolines. The derivatives of bicyclic naphthenic and aromatic hydrocarbons boil above the range of light gasolines and can be present only in heavy ends and heavy naphthas. Thus it is mainly the derivatives of cyclopentanes, cyclohexane, and benzene that represent the cyclic hydrocarbons of straight-run gasolines. The non-hydrocarbon constituents, mostly sulphur compounds, are present usually in small quantities, below 1% of the total.

Table V presents the summarized data on the content of paraffins, naphthenes, and aromatics in various straight-run gasolines.

TABLE V

Chemical Composition of Straight-Run Gasolines

Crude oil	*Sp. gr.* (D_{15})	*End-point* (°C.)	*% by wt. of* *Aromatic*	*Naphthenes*	*Paraffins*
Pennsylvania	0·732	207	7	18	75
Oklahoma City, Okla.	0·739	177	10	29	61
Tonkawa, Okla.	0·736	150	9	35	56
Tonkawa, Okla.	0·740	210	12	37	49
East Texas	0·714	159	6	42	52
Mexia, Texas	0·750	150	22	21	57
Rodessa, La.	0·719	160	10	20	70
Sante Fe Springs, Calif.	0·735	151	10	50	40
Kettleman Hills, Calif.	0·720	151	8	45	47
Signal Hill, Calif.	0·735	153	6	52	42
Huntington Beach, Calif.	0·727	155	7	49	44
Turner Valley, Canada	0·726	150	11	38	51
Portero, Mexico	0·727	200	9	35½	55½
Baku (Surachany)	0·760	175	3	71	26
Grozny (New Field)	0·722	175	6	29	65
Maikop	0·751	200	16	38	46
Merisor, Rumania	0·736	150	8	53½	38½
Bucsani, Rumania	0·736	150	12	30	54
Grabovnika, Poland	0·744	180	10	27	63

Paraffins and naphthenes are the main components of straight-run gasolines. The percentage of those hydrocarbons depends upon the crude oil: paraffin-base and mixed-base crudes produce gasolines rich in paraffins (Pennsylvania, Oklahoma City, Tonkawa, Rodessa, Grozny, Poland). The proportion of paraffins in such gasolines is above 50% and may be as high as 70%. The intermediate type with a paraffin content of about 50% is also quite common; such gasolines contain about 40% naphthenes (Texas, California, Mexico, Russia). Highly naphthenic gasolines, containing 60% or more naphthenes, are comparatively rare (Surachany and a few California gasolines). Gasolines rich in aromatics, containing more than 20% aromatics, are also rare (Mexia, Conroe, Borneo).

Paraffins of straight-run gasolines belong mostly to the normal or slightly branched types (Table VI, data by Forziati *et al.* [12, 1943]). Michigan straight-run gasoline is particularly rich in normal paraffins. Some California gasolines have a greater proportion of isoparaffins. Paraffins of Yates and Winkler (Texas) straight-run gasolines are predominantly of the iso-structure. The same table, as well as other data, shows that the distribution of cyclohexane and cyclopentane derivatives in straight-run gasolines varies from one crude to another.

The distribution of paraffins, naphthenes, and aromatics in various fractions of straight-run gasolines is illustrated

TABLE VI

Chemical Composition of Light Paraffin-Naphthene Fraction, 40° to 102° C.

Gasoline	% by vol.			
	Normal paraffins	*Iso-paraffins*	*Cyclo-pentanes*	*Cyclo-hexanes*
Ponca, Okla. . . .	35·7	20·5	23·4	20·4
East Texas . . .	24·7	27·3	26·0	22·0
Bradford, Pa. . . .	34·4	32·2	13·4	20·0
Greendale-Kaw Kawlin, Mich.	63·1	13·2	8·0	15·7
Winkler, Texas . . .	9·5	61·6	8·4	20·5
Midway, Calif. . . .	10·0	21·5	41·0	27·5
Conroe, Texas . . .	18·2	20·3	17·3	44·2

by the data [21, 1943] of Table VII. The percentage of aromatics increases with increasing boiling-range of the fraction. On the contrary, the percentage of paraffins, very high in low-boiling fractions, decreases steadily with increasing boiling-range. The percentage of naphthenes usually increases slightly with increasing boiling-range or remains almost constant.

TABLE VII

Chemical Composition of Fractions of Pennsylvania Straight-Run Gasoline

Fraction, °C.	Percentage of		
	Aromatics	*Naphthenes*	*Paraffins*
Gasoline (38–207) . .	7	18	75
38–70	0	3	97
70–100	4	18	76
100–150 . . .	8	22	70
Bottoms	12	26	62

It is understood that the above conclusions concern fractions of comparatively large boiling-ranges, as, for instance, from 30° to 50° C. The content of paraffins and other hydrocarbons in very narrow fractions depends upon the content of individual hydrocarbons and does not conform to the regularities of the large fractions.

Individual hydrocarbons of straight-run gasolines have been studied for more than 80 years. Beilstein, Aschan, Markovnikoff, Zelinsky, Young, and Mabery contributed much to the knowledge of these hydrocarbons in the early stages of these extensive investigations. The importance of these investigations cannot be underestimated. As a matter of fact, the present knowledge of the hydrocarbons of gasolines does not differ fundamentally from the general conceptions developed by the authors cited.

A qualitative picture of the composition of gasolines was well established on the basis of the extensive work performed by these and many other workers. Quantitative methods of separating hydrocarbons were developed much later, during the last 15 years. The most successful and complete separation of individual hydrocarbons has been carried out by the National Bureau of Standards for a gasoline from Ponca City (Oklahoma) crude. This may be considered as a typical Mid-Continent crude of the so-called mixed-based type. The methods used for quantitative separation of hydrocarbons were physical (fractional distillation, azeotropic distillation, crystallization, adsorption, solvent extraction) and chemical (sulphonation, nitration, &c.). The separation was much closer than in all other similar studies. As a matter of fact, many hydrocarbons separated from the Ponca City gasoline were obtained in a purer state than they were known before this investigation. Over 75% of the gasoline boiling between 55° and 145° C. and over 33% of the naphtha boiling between 145° and 180° C. were assigned to the individual hydrocarbons separated. The results are summarized in Tables VIII and IX. Table IX includes latest data published in 1947 [11*a*, 14*a*, 41*a*].

Rossini *et al.* [42, 1942] and Forziati *et al.* [12, 1943] have published the data on the composition of a series of most typical straight-run gasolines: Ponca (paraffinic), Conroe (high aromatic), Michigan (high paraffinic), Winkler (high isoparaffinic), Midway (high naphthenic), and Pennsylvania (high paraffinic). These gasolines were investigated by simplified methods. They were separated by adsorption with silica gel into naphthenic-paraffinic and aromatic parts, which were fractionated in highly efficient columns. By this method separation is greatly improved, because aromatic hydrocarbons do not interfere with the

TABLE VIII

Hydrocarbons isolated from (Depentanized) Ponca City Straight-Run Gasoline

Hydrocarbon	*Boiling-point at 760 mm. (°C.)*	*% by vol. of crude oil**
Paraffins		
2, 3-Dimethylbutane	58·0	0·06
2-Methylpentane	60·4	0·12
3-Methylpentane	63·3	0·25
n-Hexane	68·7	0·7
2, 2-Dimethylpentane	78·9	0·04
2-Methylhexane	89·7	0·35
3-Methylhexane	92·0	0·2
n-Heptane	98·4	1·1
2-Methylheptane	117·2	0·5
n-Octane	125·4	1·0
2, 6-Dimethylheptane	135·2	0·1
Isononane (probably 2, 3-dimethylheptane) .	140·7	0·05
4-Methyloctane	142·4	0·06
2-Methyloctane	143·3	0·2
3-Methyloctane	144·2	0·06
n-Nonane	150·7	1·0
n-Decane	174·0	0·8
Naphthenes		
Methylcyclopentane	71·8	0·25
Cyclohexane	80·8	0·35
1, 1-Dimethylcyclopentane	87·5	0·05
trans-1, 3-Dimethylcyclopentane . . .	90·9	0·2
trans-1, 2-Dimethylcyclopentane . . .	91·9	0·3
Methylcyclohexane	100·8	0·3
trans-1, 3-Dimethylcyclohexane . . .	121·0	0·15
Ethylcyclohexane	131·8	0·1
Nononaphthene (probably cyclopentane structure)	136·7	0·1
1, 2, 4-Trimethylcyclohexane . . .	141·2	0·1
Aromatics		
Benzene	80·2	0·08
Toluene	110·5	0·3
Ethylbenzene	136·1	0·03
p-Xylene	138·4	0·04
m-Xylene	139·2	0·12
o-Xylene	144·4	0·22
Isopropylbenzene	152·4	0·03 (0·07)†
1, 3, 5-Trimethylbenzene (mesitylene) . .	164·6	0·02 (0·12)†
1, 2, 4-Trimethylbenzene (pseudocumene) .	169·2	0·2 (0·51)†
1, 2, 3-Trimethylbenzene (hemimellitene) .	176·1	0·06

* The actual percentage may be 1–1⅔ times greater than the below figures.

† Latest data [11*a*, 1947].

TABLE IX

Hydrocarbons isolated from Ponca City Straight-run Gasoline, Latest Data, 1946–8

Hydrocarbon	*Boiling-point at 760 mm. (°C.)*	*% by vol. of crude oil*
Paraffins		
2, 2-Dimethylhexane	106·8	0·01
2, 3-Dimethylheptane	140·7	..
4-Methylnonane	165·7	..
2-Methylnonane	166·8	..
3-Methylnonane	167·8	..
Undecane	195·4	..
Naphthenes		
trans-1, 3-Dimethylcyclopentane	90·9	..
trans-1, 2-Dimethylcyclopentane	91·9	..
Ethylcyclopentane	103·5	0·16
1, 1, 3-Trimethylcyclopentane	104·9	0·30
1, 1-Dimethylcyclohexane (not definitely identified)	119·8	..
trans-1, 2-Dimethylcyclohexane (not definitely identified)	123·4	..
Monocyclic C_9H_{18}	145·6	..
Bicyclic C_9H_{16}	146·7	..
Aromatics		
n-Propylbenzene$_4$	159·5	0·09
1-Methyl-3-ethylbenzene	161·6	0·17
1-Methyl-4-ethylbenzene	162·5	0·06
1-Methyl-2-ethylbenzene	165·1	0·09
Tert.-butylbenzene	169·0	0·01

fractionation of paraffins and naphthenes. The narrow fractions obtained by fractionation contained a limited number of individual hydrocarbons and were analysed mostly by the refractive index and refractive-intercept methods. The results are given in Table X.

Gooding *et al.* of the Bureau of Mines [15, 1946] determined individual hydrocarbons in the fraction boiling from 97° to 242° F. (36° to 117° C.) for various crudes. The method used was similar to that of the Bureau of Standards, without, however, separation of aromatic and naphthenic-paraffinic parts: fractional distillation and determination of individual hydrocarbons in narrow fractions by specific dispersion and refractive intercept. The accuracy of the paraffin or naphthene content has been estimated as 10%. Table XI includes the results obtained.

The composition of straight-run gasolines seems to be simpler than might be expected on the basis of numerous isomers which might be present in the boiling-range of the gasolines. As Rossini stated for the Ponca City gasoline, 'Three-fourths of the gasoline fraction 55°–145° C. is constructed by approximately 31 hydrocarbons, one-half by about 8, one-third by 4, and one-fifth by 2. That is to say, while there may actually be thousands of hydrocarbons in this fraction, the major part of the material is made up of a rather small number of constituents' [41, 1937]. Approximately 50% of the 55–180° C. gasoline is composed of about 12 hydrocarbons.

Normal paraffins occur in most gasolines and predominate in many of them. Nevertheless, numerous isomeric paraffins have been isolated. As a rule, slightly branched paraffins, such as monomethylpentane, monomethylhexane, predominate over highly branched.

Cyclohexane, methyl-, dimethyl-, and trimethylcyclohexanes, methyl-, dimethyl-, and trimethylcyclopentanes predominate among the naphthenic hydrocarbons present in gasolines. Cyclopentane is represented in a minute amount. Naphthenic hydrocarbons with another number of carbon atoms in the ring than 5 or 6 so far have not been detected in gasolines, even in small quantities. The presence of naphthenes with 3 or 4 carbon-atom cyclic structure, as well as of naphthenes with a bridge in the ring, seems unlikely in view of the absence of optic exaltation in straight-run gasolines and their fractions free of aromatics.

The aromatic hydrocarbons are represented by all known hydrocarbons boiling in the range of gasolines. The content

TABLE X

Hydrocarbons in Straight-run Gasolines, U.S.A.
Boiling-range 40° to 180° C.

Hydrocarbon	*% by vol.*						
	Ponca, Okla.	*East Texas*	*Bradford, Penn.*	*Greendale, Mich.*	*Winkler, Texas*	*Midway, Calif.*	*Conroe, Texas*
Cyclopentane	0·15	0·31	0·23	0·26	0·31	0·79	0·27
2, 2-Dimethylbutane	0·12	0·19	0·16	0·05	0·24	0·27	0·20
2, 3-Dimethylbutane	0·25	0·46	0·47	0·32	0·55	0·33	0·33
2-Methylpentane	1·24	2·67	3·73	1·44	1·76	1·83	1·61
3-Methylpentane	1·15	2·03	2·22	0·95	4·40	1·24	1·12
n-Hexane	5·98	5·34	6·31	12·11	1·19	2·04	2·48
Methylcyclopentane	2·88	4·03	1·50	1·68	1·63	4·33	2·97
2, 2- and 2, 4-Dimethylpentane	0·31	1·01	0·94	0·32	0·87	0·49	0·42
Cyclohexane	2·36	2·04	1·95	2·14	0·64	2·69	4·34
1, 1-Dimethylcyclopentane	0·54	0·61	0·58	0·39	0·65	0·62	0·45
2, 3-Dimethylpentane and 2-methylhexane	3·58	3·91	4·00	2·03	4·70	2·33	2·48
trans-1, 3-Dimethylcyclopentane	3·94	4·34	1·64	0·73	1·62	5·66	1·56
trans-1, 2-Dimethylcyclopentane	1·35	1·74	1·54	0·26	1·25	2·21	0·41
3-Methylhexane	1·09	1·29	1·65	0·39	3·87	0·65	0·47
n-Heptane	7·55	5·14	7·71	14·19	1·34	1·28	3·47
Methylcyclohexane	5·39	7·30	6·27	4·42	1·55	6·47	10·10
Benzene	0·46	0·21	0·19	0·63	0·13	0·20	1·23
Toluene	1·53	1·73	1·52	1·77	0·26	1·28	7·37
Ethylbenzene	0·56	0·68	0·26	0·36	0·23	0·66	0·93
p-Xylene	0·29	0·50	0·50	0·28	0·36	0·44	1·78
m-Xylene	1·53	1·93	1·83	1·20	0·24	1·08	6·10
o-Xylene	0·80	0·88	0·63	0·52	0·09	0·63	2·04
Isopropylbenzene	0·21	0·16	0·10	0·13	0·30	0·26	0·32
n-Propylbenzene	0·24	0·23	0·16	0·14	0·20	0·21	0·42

TABLE XI

Volume % of Individual Hydrocarbons in the 97° to 243° F. Boiling-range for Several Representative Naphthas

Hydrocarbons	*Coalinga*	*Conroe*	*Hastings*	*Jennings*	*K.M.A. Strawn*	*Old Ocean*	*Saxet*	*Segno*	*Tom O'Connor*	*Wade City*
n-Pentane*	0·44	0·33	0·89	1·12	0·40	0·36	1·11	0·55	None	1·28
Cyclopentane	1·76	0·96	1·23	0·67	1·25	0·85	0·73	1·08	1·04	1·36
2, 2-Dimethylbutane	0·25	0·39	0·78	0·42	0·16	0·58	0·32	0·74	0·60	0·57
2, 3-Dimethylbutane	2·21	1·46	1·97	2·05	1·74	1·88	1·25	1·94	2·09	1·27
2-Methylpentane	2·56	2·89	2·16	3·47	4·39	5·23	1·33	3·71	4·61	1·14
3-Methylpentane	1·89	2·09	1·81	1·03	3·80	3·36	0·88	2·22	2·62	1·52
n-Hexane	7·75	6·44	5·18	9·15	12·71	10·18	2·29	8·84	7·76	2·04
Methylcyclopentane	10·29	6·51	7·42	5·01	7·52	5·42	5·52	6·40	6·70	7·39
2, 2-Dimethylpentane 2, 4-Dimethylpentane	0·51	0·96	2·55	1·46	0·79	1·52	3·51	1·38	1·72	2·27
Benzene	2·22	3·27	0·16	3·61	0·59	2·28	None	1·82	0·58	0·38
Cyclohexane	7·63	10·40	13·66	7·13	4·68	7·30	15·07	9·64	10·94	14·93
1, 1-Dimethylcyclopentane	1·17	0·35	0·70	1·00	0·45	0·83	1·30	0·59	0·68	0·96
2, 3-Dimethylpentane 2-Methylhexane	2·69	3·45	4·53	6·14	5·81	6·71	2·39	5·32	5·79	2·27
trans-1, 3-Dimethylcyclopentane	4·92	2·62	5·78	2·53	7·08	3·87	4·33	2·98	4·36	3·97
trans-1, 2-Dimethylcyclopentane	7·05	1·59	2·35	1·02	5·29	1·41	3·12	1·29	2·64	3·94
3-Methylhexane	3·30	1·90	1·49	2·25	3·90	2·88	1·25	2·01	3·29	1·32
n-Heptane	5·94	6·90	2·43	8·42	11·32	10·92	1·69	7·96	4·96	0·86
Methylcyclohexane	14·55	22·00	32·39	18·07	12·29	17·20	37·48	21·58	23·02	35·62
Ethylcyclopentane	4·38	2·03	3·58	2·34	3·65	3·48	4·09	2·70	3·22	5·16
2, 2-Dimethylhexane	0·57	0·71	0·77	2·39	0·93	1·51	1·35	1·27	1·51	1·39
2, 5-Dimethylhexane 2, 4-Dimethylhexane	0·56	2·70	2·02	2·13	0·51	1·04	2·11	1·69	0·33	1·19
Toluene	7·94	16·19	0·77	12·02	2·57	5·87	None	9·61	3·39	2·64
Trimethylcyclopentanes (?)	7·23	3·56	3·05	3·71	4·56	3·38	4·42	2·56	3·58	3·69
2, 3-Dimethylhexane	1·30	0·22	1·33	2·39	2·49	1·45	1·66	1·87	3·39	1·23
A trimethylcyclopentane (?)	0·89	0·08	1·00	0·47	1·12	0·49	2·80	0·25	1·18	1·61
Total	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00

* *n*-Pentane boiling below 97·0° F. not included in these figures.

of benzene is usually very small, and other benzene homologues are present in larger amounts.

The content of toluene may be comparatively large in certain straight-run gasolines, such as Conroe or Tomball. For manufacturing toluene from petroleum, the content of methylcyclohexane, easily convertible into toluene by the hydroforming process, is of importance. The data of Table XII include the percentage of toluene and methylcyclohexane in several crudes, according to Fischer and Welty [11, 1944].

TABLE XII

Content of Toluene and Methylcyclohexane in Crude Oils

Crude oil	*% by vol. of* Toluene	*% by vol. of* Methylcyclohexane (+ethylcyclopentane up to 15–20%)
Texas coastal	0·03	1·2
Conroe, Texas	2·0	2·5
East Texas	0·40	1·7
Kettleman Hills, Calif.	0·70	2·1
Midway light, Calif.	0·02	0·52
No. Sweden mixture	0·80	3·7
Panhandle, Texas	0·22	2·3
Pecos, Texas.	0·03	1·0
Refugio, Texas	0·26	2·9
Salt Flat-Regan, Texas	0·19	1·5
Santa Maria, Calif.	0·14	0·79
Sugarland, Texas	None	2·1
Tomball mixture, Texas	1·1	2·1
Tinsley, Mississippi	0·08	0·65
West Texas	0·50	1·3

Of the aromatics C_8H_{10}, metaxylene usually predominates over other isomers.

The occurrence and distribution of individual hydrocarbons in straight-run gasolines and crude oils has no correlation with the thermodynamic stability of hydrocarbons. For instance, the predominance of normal paraffins in crude oils does not correspond to the relative instability of such hydrocarbons compared to branched isomers under the low-temperature conditions in which the crude oils were undoubtedly formed. It is known that at temperatures up to at least 200° C. the branched paraffins are more stable than corresponding normal hydrocarbons, and largely predominate over normal paraffins under equilibrium conditions.

Almost all petroleum hydrocarbons and compounds are thermodynamically unstable and exist only because of the inactivity of the hydrocarbons in question. The free energy of hydrocarbons, compared with carbon and hydrogen, is much greater than, for instance, that of any isomerization process. The isomerization of petroleum hydrocarbons at low temperatures and in the absence of specific catalysts would be just as improbable as the spontaneous decomposition of hydrocarbons into carbon and hydrogen. By the same reasoning, the absence of olefines and other unsaturates in crude oils is due not to their particular thermodynamic instability but to their activity. Crude oils consist of hydrocarbons and compounds which are thermodynamically unstable but kinematically inactive.

Synthetic Gasolines. In contrast to straight-run gasolines, synthetic gasolines are produced from petroleum oils by means of various chemical reactions effected by temperature, catalysts, or temperature and catalysts. Cracked gasoline is the most known type of such synthetic gasolines.

In addition to the paraffins, naphthenes, and aromatics, present in straight-run gasolines, cracked gasolines contain unsaturates, including open-chain and cyclic olefines, diolefines, and cyclic hydrocarbons with olefinic side chains. The chemical composition of cracked gasolines depends not only upon the nature of the charging-stock but, to a greater degree, upon the type and conditions of the cracking process. Table XIII summarizes the data on the chemical composition of cracked gasolines.

TABLE XIII

Chemical Composition of Cracked Gasolines
(End-point 400° F.)

Charging-stock	% by weight *Aro-matics*	*Unsatu-rates*	*Naph-thenes*	*Paraf-fins*
Mixed-phase Non-catalytic Process				
W. Texas topped crude	13·1	30·8	..	..
Panhandle gas oil	10·5	32·8	..	..
Seminole fuel oil	9·0	29·1	..	..
Smackover crude	16·0	29·1	..	..
Panuco crude	15·6	27·3	..	..
Pennsylvania crude	7·1	34·6	..	..
Grozny waxy gas oil	7	31	16	45
Surachany waxy fuel oil	4	39	13	44
Oklahoma City gas oil	10	39	16	35
Light gas oil, mixed-base	8·5	30	15	46·5
Heavy gas oil, same	6·5	41	9	43·5
Residuum, same	6	45	8	41
Kerosine naphthenic	9	24	35	32
Residuum naphthenic	6·5	36·5	11·5	46
Vapour-phase Cracking				
Mixed gas oil (DeFlorez)	16	49	25	10
Gas oil (Gyro)	23	45	14	19
Catalytic (Houdry) Process				
Gas oil, low space rate (1:1)	15	18	23	44
E. Texas naphtha (reforming)	17·3	10·0	23·4	49·3
Gas oil, A.P.I. 31°	16	8	21	47
Reduced coastal crude	18	24	24	34
Second pass	33	5	14	48

The distribution of hydrocarbons in the fractions of cracked gasolines gives approximately the same pattern for all cracking processes. The content of unsaturates and, to a lesser degree, of paraffins decreases with increasing boiling-range of the fraction, while the content of aromatics steadily and rapidly increases.

The chemical composition of cracked gasolines formed by the mixed-phase (non-catalytic) process (under pressure) depends upon the nature of the charging-stock. The naphthenic and asphaltic crudes (Smackover, Panuco) yield gasolines having a higher content of naphthenes and aromatics. The content of unsaturates varies in a comparatively narrow range from 30–40%.

The composition of reformed gasolines is close to that of mixed-phase cracked gasolines, but the content of aromatics is appreciably higher.

Polyformed and hydroformed gasolines contain a large percentage of aromatics. The polyforming or gas reversion process is carried out in the presence of hydrocarbon gases under rather severe temperature conditions, resulting in an increased proportion of aromatics. The hydroforming process is accompanied by dehydrogenation of cyclohexanes and by partial cyclization of paraffins into aromatics in the presence of a molybdena catalyst, which results in a high percentage of aromatics, amounting to 50% for some selected charging-stocks.

Vapour-phase cracked gasolines have a high percentage of olefines and aromatics. The percentage of aromatics is not necessarily great in these gasolines, unless the temperature of the process is very high, above 600° C. (1,112° F.). Such gasolines are also comparatively rich in diolefines, cyclic olefines, and styrene.

Catalytically cracked gasolines (produced in the Houdry, T.C.C., or 'fluid catalyst' processes) differ substantially in their chemical composition from thermally cracked gasolines. In general, the content of unsaturates is comparatively small, which causes the great stability of such gasolines. The aromatic content is larger than in thermally cracked gasolines but is not particularly high, usually not exceeding 15–20% on the average. Catalytic reforming, or so-called two-pass catalytic cracking, produces gasolines with an aromatic content amounting to 25–30% or more. The content of paraffins is usually high, approximately 45–50%. As will be seen later, the paraffins of catalytically cracked gasolines are predominantly isoparaffins causing high-octane numbers.

It should be pointed out, however, that the composition of catalytic gasolines depends not only upon conventional cracking conditions, such as temperature, pressure, charging-stock, but also upon factors relating to the catalyst. The relative amount of catalyst with reference to the charging-stock bears strongly on the chemical composition of gasolines obtained. Another factor is the nature and activity of the catalyst, which changes during cracking, being great in the early stage and decreasing rapidly with soaking time because of deposition of coke on the catalytic surface. It is evident that the distinction between thermally and catalytically cracked gasolines becomes less and less significant at low ratios of catalyst to charging-stock or/and in advanced stages of catalytic cracking, when the catalyst is appreciably deactivated. Highly unsaturated gasolines containing as much as 50% unsaturates can be produced under such conditions. On the contrary, gasolines high in aromatics and low in unsaturates are obtained at higher ratios of catalyst to charging stock, at low space rates and at higher temperatures.

The catalytically cracked gasolines from the cycloversion process, produced at high temperatures up to 1,200° F. in the presence of steam, are more unsaturated than other catalytically cracked gasolines produced at much more moderate temperatures (from 850 to 950° F.). The content of unsaturates in the cycloversion gasolines was reported as high as 60–80% (calculated on the basis of bromine numbers from 90 to 125 and possibly somewhat exaggerated due to secondary reactions on determining the bromine numbers).

The knowledge of individual hydrocarbons in cracked gasolines is very meagre. Of the aromatic hydrocarbons, benzene occurs in an insignificant proportion in commercial mixed-phase and catalytically cracked gasolines, averaging 0·2 and 1·0% respectively. The proportion of toluene and xylenes (+ethylbenzene) is much greater, averaging 1 and 1½–2% for thermal and 5 and 10% for catalytic gasolines with reference to the total gasoline (E.P. 350° F.). The toluene and xylene content in polyformed gasolines may be as high as 4 and 7% respectively. The yield of toluene may be still higher by the hydroforming process, particularly from special naphthas rich in methylcyclohexane. Commercial production of toluene by the two processes during the last war was carried out on a very large scale. Metaxylene predominates over other isomers of the aromatics C_8H_{10} (Table XIII*a*). Orthoxylene, constituting 20% of all xylenes produced by hydroforming, is oxidized commercially for manufacturing phthalic anhydride [5, 1946].

With the exception of certain C_4 and C_5 unsaturates, no other individual olefines or unsaturates were positively identified or separated from cracked gasolines. Normal butenes predominate over isobutene in both thermal and catalytic gasolines; butene-2 predominates over butene-1. Frey *et al.* [14, 1940] gave the following composition of the C_5-cracked (non-catalytic pressure cracking) fraction:

Tertiary pentenes	16%
Pentene-1	11%
Pentene-2	20%
Pentanes (*n* and *iso*)	53%

Bates *et al.* [3, 1942] fractionated the hexane fraction of a thermally cracked gasoline and identified the following isomers:

n-Hexane	63%
2-Methylpentane	18%
3-Methylpentane	16%
2, 3-Dimethylbutane	3%

Normal pentane and hexane predominate over the corresponding isomers in thermally cracked gasolines. The heptane fractions of thermally cracked gasolines were studied by Brown *et al.* [3*b*, 1948]; *n*-heptane, methylhexanes, methylcyclohexane, and dimethylcyclopentanes predominate in these fractions.

The paraffin hydrocarbons of catalytically cracked gasolines (Houdry process) were studied by Bates *et al.* [3, 1942]. A typical analysis of light ends of an unstabilized Houdry gasoline gives the following results:

n-Butane	2·2%	*n*-Pentane	1·3%
Isobutane	10·9%	Isopentane	10·3%
n-Butene	5·9%	Total pentenes	7·3%
Isobutene	1·7%	C_6 and heavier	60·3%

The high percentage of isobutane and isopentane should be pointed out. The higher fractions of catalytic gasolines, C_6 and C_7, freed of unsaturates and aromatics were also studied. The distribution of various heptanes in the heptane cut is as follows:

2, 2-Dimethylpentane 2, 4-Dimethylpentane 3, 3-Dimethylpentane 2, 2, 3-Trimethylbutane	6%
2, 3-Dimethylpentane 2-Methylhexane 3-Methylhexane 3-Ethylpentane	89%
n-Heptane 2, 2, 4-Trimethylpentane	5%

The composition of C_6 and C_7 paraffinic fractions also shows that the branched paraffins predominate over normal hydrocarbons, and also that isomers with a moderate degree of branching predominate over those that are highly branched. Glasgow *et al.* [14*b*, 1948] reported on the chemical composition of a two-pass catalytically cracked gasoline. The data are summarized in an abbreviated form in Table XIII*a*.

Other synthetic gasolines include alkylates and polymer gasolines synthesized from cracking gases. The average composition of a commercial alkylate from isobutane and C_4 olefines may be represented as follows:

Isopentane	up to 10%
n-pentane	less than 1%
Isohexanes	about 5%
Isoheptanes	about 5%
2, 2, 4-Trimethylpentane	from 25 to 45%
2, 2, 3-Trimethylpentane	less than 3%
2, 3, 3-Trimethylpentane	from 10 to 20%
2, 3, 4-Trimethylpentane	from 15 to 30%
Dimethylhexanes and higher	up to 20%

TABLE XIII*a*

Chemical Composition of Depentanized Catalytically Cracked Gasoline

Hydrocarbon	*% by volume*
Cyclopentane and 2, 2-Dimethylbutane	0·40
2, 3-Dimethylbutane	1·95
2- and 3-Methylpentane	11·55
n-Hexane	1·4
Methylcyclopentane	3·9
Benzene	1·8
2, 2- and 2, 4-Dimethylpentane, cyclohexane	1·3
1, 1-, trans-1, 3 and trans-1, 2-Dimethylcyclopentane	3·9
2, 3-Dimethylpentane, 2- and 3-methylhexane	6·1
n-Heptane	1·3
Methylcyclohexane	2·6
Ethylcyclopentane, trimethylcyclopentanes, 2, 2-, 2, 5-, 2, 4-dimethylhexane	2·5
Toluene	8·5
Trimethylcyclopentanes, 3, 3- and 2, 3-dimethylhexane	1·2
2-, 4-, 3-Methylheptane, dimethylcyclohexanes	5·8
n-Octane	0·8
Dimethylheptanes, methyloctanes	2·6
Ethylbenzene	1·6
p-Xylene	3·4
m-Xylene	8·8
o-Xylene	4·0
n-Nonane	0·7
n and Isopropylbenzene	0·4
1-Methyl-3-ethyl- and 1-methyl-4-methyl-benzene	3·6
1, 3, 5-Trimethyl- and 1-methyl-2-ethyl-benzene	2·5
tert-Butyl- and 1, 2, 4-trimethyl-benzene	3·6
Higher aromatics	1·7
Unidentified paraffins	2·8
Unidentified naphthenes	4·9
Olefins	4·4
Total	100·0

If the alkylate is produced from C_3 and C_4 olefines, the proportion of isoheptanes will be much higher, depending upon the content of propene in the gas. In addition to the composition of the charging-stock (olefines, isobutane, or isopentane), the composition of the alkylate is affected to a lesser degree by the nature of the catalyst (sulphuric acid, hydrofluoric acid, aluminium chloride), temperature, reaction time, and ratio of isoparaffin to olefines in the reactor.

While alkylation of isobutane with any butene produces invariably a complex mixture of various isomers, the alkylation of isobutane with ethene gives predominantly 2, 3-dimethylbutane (diisopropyl) over a heterogeneous catalyst, e.g. aluminium chloride [1, 1946], and 2, 2-dimethylbutane (neohexane) in the presence of homogeneous catalysts [38, 1946], or non-catalytically [37, 1939] at high temperatures.

Polymer gasolines, produced by catalytic polymerization of propene and butenes (cracking gases), have a high content up to 80–85% by volume of unsaturates, predominantly olefines, but also some paraffins, naphthenes, and aromatics. Tongberg *et al.* [50, 1937] found that heptenes and octenes predominate over other olefines, as could be expected. Aromatics, cyclic olefines, and diolefines are found to be present in comparatively small amounts. No individual hydrocarbons were identified in polymer gasolines.

Catalytic polymerization of isobutene under mild temperature conditions produces 2, 4, 4-trimethylpentene-1 (and less 2, 4, 4-trimethylpentene-2) almost quantitatively. Hydrogenation of this olefine gives commercial iso-octane or 2, 4, 4-trimethylpentane.

Gas Oils and Kerosines

Straight-run Gas Oils. The ring analysis of straight-run kerosines and gas oils gives figures which differ widely for products from paraffinic and asphaltic crudes (Table XIV). The percentage of paraffinic elements or side chains is as

TABLE XIV

Ring Analysis of Straight-run Gas Oils

	Paraffin-base	*Asphaltic base*
Sp. gr. at 15° C.	0·840	0·900
Boiling-range (°C.)	240–375	240–375
Aniline point (°C.)	80	55
Cetane no.	60	35
Percentage of:		
aromatic rings	8	22
naphthenic rings	15	35
paraffinic side chains	77	43
Average no. of rings per molecule	1·5	2·5

high as 70 to 80% in kerosines and gas oils from paraffin- and some mixed-base crudes (Pennsylvania, Michigan, various Mid-Continent crudes). Correspondingly the percentage of rings is small in such distillates, and the average number of rings per molecule is less than 2. The average length of the paraffinic side chains is as great as C_{10}. The percentage of paraffinic side chains in 'naphthenic' or asphaltic kerosines and gas oils (California, various Gulf Coast crudes) may be as low as 40. The ring content is correspondingly high. The percentage of naphthenic rings is usually much greater than that of aromatic rings. The average number of rings per molecule is from 2 to 3, indicating the predominance of polycyclic hydrocarbons. The average length of the chains does not exceed C_5.

The percentage of paraffinic elements or side chains, given above, includes free paraffin hydrocarbons and paraffinic side chains connected with cyclic structures. The content of paraffin hydrocarbons in gas oils cannot be determined with any degree of accuracy; approximately evaluated, it may vary in a broad range from 40–50% for paraffinic gas oils to 0–10% for highly 'naphthenic' or asphaltic gas oils.

The content of aromatic hydrocarbons in gas oils can be determined with sufficient accuracy. The summarized data are given in Table XV.

TABLE XV

Content of Aromatic Hydrocarbons in Straight-run Gas Oils

Gas oil	*Boiling-range (°C.)*	*Sp. gr. 15° C.*	*% of aromatics by weight*
Penna	200–300	0·803	10
Tonkawa, Okla.	"	0·823	23
Mexia, Texas	"	0·807	12
Huntington Beach, Calif.	"	0·838	27
Portero, Mexico	170–300	0·807	19
Baku (Surachany)	200–350	0·835	17
Grozny (New Field)	200–350	0·830	17

Few individual hydrocarbons are separated from low-boiling fractions of kerosines and gas oils. Mair and Streiff [29, 1940] isolated normal dodecane, naphthalene, and both methylnaphthalenes from the Ponca City kerosine fraction 200–230° C. (Table XVI). The high proportion of normal dodecane and other normal paraffins seems to be significant for fractions produced from paraffin and mixed-base crudes. In a later communication the same authors [29, 1941] reported on the isolation of 1, 2, 3, 4-tetramethylbenzene and both methyltetralins from the above Ponca City fraction; *n*-amyl benzene, two dimethyl propyl benzenes, trimethyl propyl benzene, and phenylcyclopentanes were provisionally identified in the same kerosine fraction [41*a*, 1947]. Hufferd and Kranz [20, 1939] fractionated a Pennsylvania gas oil boiling between 150° and 350° C. with columns of 30–2% theoretical plates collecting 1% fractions. Refractive indices and melting-points determined for each fraction showed that every possible normal paraffin occurs in the gas oil.

TABLE XVI

*Hydrocarbons isolated from Ponca City Straight-run Kerosine Fraction, 200–230° C. Cut**

Hydrocarbon	*Boiling-point (°C. at 1 atm.)*	*% by weight*	
		In fraction	*In crude oil*
n-Dodecane	216·26	13·6 ± 0·8	1·0
1, 2, 3, 4-Tetramethylbenzene	205·4	1·06 ± 0·07	0·078
Tetralin	207·57	0·27 ± 0·03	0·020
1-Methyltetralin	234·35	0·65 ± 0·12	0·048
2-Methyltetralin	224·03	0·68 ± 0·06	0·050
Naphthalene	217·96	0·46 ± 0·04	0·034
1-Methylnaphthalene	244·78	0·84 ± 0·06	0·062
2-Methylnaphthalene	241·14	1·80 ± 0·10	0·132
Total	..	19·4 ± 0·8	1·4

* Method of determination: fractionation by distillation and crystallization, solvent treatment, and other physical and chemical methods.

The presence of naphthalene and particularly methylnaphthalenes in kerosine fractions is quite common in various crudes. In addition to naphthalene and both methylnaphthalenes, the following derivatives were isolated by various authors: dimethylnaphthalenes (1, 2; 1, 3; 1, 6; 1, 7; 2, 3; 2, 6), trimethylnaphthalenes (1, 3, 6; 2, 3, 6), phenanthrene.

The homologues of tetralin and decalin seem to be largely represented in straight-run kerosines and gas oils, although only tetralin and its methyl derivatives have so far been separated.

Olefines and other unsaturates are absent in straight-run gas oils.

Thus paraffins and alkylated monocyclic, and dicyclic naphthenes and aromatics are unquestionably the main constituents of gas oils. As has been stated above, paraffins may be absent in high-boiling fractions of gas oils from naphthenic or asphaltic crude oils.

Only condensed polycyclic aromatic and hydro-aromatic hydrocarbons have so far been identified in gas oils. The question of the presence of the derivatives of diphenyl and dicyclohexyl, diphenyl- or triphenylmethane, &c., is not at all clear. Grosse and Mavity [16, 1939] dehydrogenated a solvent extract from a kerosine fraction, 200–250° C., of Placedo crude over a chromia catalyst and claimed that a substantial quantity of diphenyl, as well as of dimethylnaphthalenes, was isolated from the reaction products. These hydrocarbons are considered to be a result of dehydrogenation of the dicyclohexyl and dimethyldecahydronaphthalenes present in the virgin kerosine fraction.

It is certain, however, that the derivatives of condensed aromatics and naphthenes, such as naphthalene, phenanthrene, tetralin, decalin, &c., at least predominate in straight-run gas oils.

Synthetic Gas Oils. Synthetic gas oils are obtained as by-products or intermediate products in almost all synthetic processes, such as cracking, hydrogenation, polymerization, &c. Cracked gas oil or cracking recycle stock, the most known synthetic gas oil, is an intermediate product of cracking, commonly used for repeated cracking or recycling to obtain maximum yield of cracked gasolines. It is also widely used as a domestic fuel.

Cracked gas oils differ very substantially from straight-run distillates of the same boiling-range because of a substantial content of unsaturates, which is usually close to 20% in thermally cracked gas oils and somewhat less in catalytically cracked gas oils. The content of aromatics in cracked gas oils depends on the charging-stock, the temperature-pressure conditions of the process, and the type of cracking; it varies from 20 to 30% in commercial thermally cracked gas oils and is much higher in catalytic products of the same boiling-range.

Few individual hydrocarbons, mostly aromatics, were isolated from recycle stocks: naphthalene, methyl- and dimethylnaphthalenes, anthracene, phenanthrene, and some methyl derivatives of the last two hydrocarbons.

Lubricating Oils

Ring Analysis. The ring analysis data for various lubricating oils are summarized in Table XVII. The percentage of paraffinic elements or side chains varies from 80% in lubricating oils from Pennsylvania crudes to 40% in those from asphaltic stocks. Naphthenic rings predominate in lubricating oils from paraffin- and mixed-base crudes; in those from naphthenic and asphaltic crudes the percentage of naphthenic and aromatic rings is approximately equal. It should be pointed out that the ring content of commercial lubricating oils depends largely on the severity of treatment which removes more or less selectively aromatic hydrocarbons. Thus there is a considerable difference between the ring analysis data for original untreated stocks and for commercial lubricating oils produced therefrom.

TABLE XVII

Ring Analysis of Commercial Lubricating Oils

Lubricating oil	Gravity A.P.I.	Viscosity at 210° F. Saybolt	V.I.	Mol. weight	Rings per molecule	% of Arom. rings	% of Naph. rings	% of Paraffinic side chains
Penna S.A.E. 20	30·8	45·5	100	395	1·6	7	18	75
Penna S.A.E. 40	29·4	76·0	107	494	2·0	4	20	76
Rodessa S.A.E. 20	30·0	45·3	98·1	397	1·9	9	20	71
M.C. S.A.E. 20	25·9	49·4	67	377	2·2	11	24	65
Gulf S.A.E. 20	25·4	43·1	33	311	2·5	4	44	52
Gulf S.A.E. 40	23·0	64·0	33	378	3·0	4	43	53
Calif. S.A.E. 20	20·3	49·2	−4	330	2·9	20	32	48

The average number of rings per molecule varies from 1·5 for paraffin-base lubricating oils to 4·0–4·5 for asphaltic lubricating oils. Thus polycyclic naphthenes and aromatics predominate in lubricating oils, particularly naphthenic and asphaltic. The average length of paraffinic side chains also depends upon the origin of the lubricating oil, as well as upon the boiling-range; it varies from C_7 for asphaltic oils to C_{20} and more for viscous paraffin- and mixed-base products.

The ring structure of lubricating oils predetermines their commercial properties. The specific gravity and refractive index are high for lubricating oils with a large percentage of rings, particularly aromatic. The higher the percentage of paraffinic side chains the higher the viscosity index. At the same molecular weight or boiling-range, the greater the number of rings the higher the viscosity, because the viscosity of hydrocarbons increases with increasing number of rings at the same molecular weight. As a result, naphthenic or aromatic lubricating oils have a lower boiling-range and greater volatility than paraffin-base lubricating oils of the same viscosity. This explains the well-known fact that the flash-point is higher for the latter than for the former. The properties of paraffin- and asphaltic-base lubricating oils may be summarized as follows:

	Paraffin-base	*Asphaltic-base*
Molecular weight	350–650	200–450
Percentage of paraffinic side chains	75	45
Percentage of naphthenic-aromatic rings	25	55
Average number of rings	1·7	3·5
Specific gravity (60°/60° F.)	0·86–0·89	0·91–0·97
Viscosity at 100° F., S.U.	100–2,350	100–7,000
Viscosity at 210° F., S.U.	39–150	37–150
Viscosity index	100	−30
Boiling range at atm. pressure, °F.	750–1,400	650–1,200
Flash, °F.	390–550	335–465

The properties of mixed-base lubricating oils lie between those of paraffin- and asphaltic-base oils, but much closer to the former.

Commercial lubricating oils consist of hydrocarbons boiling in a very broad boiling-range. Fractionation by conventional methods of distillation resolves a lubricating oil into cuts or fractions differing in their boiling range or molecular weight. The ring structure of such fractions remains approximately unchanged as compared with the original oil. On the other hand, fractionation by solvent extraction separates the lubricating oil into fractions approximately of the same molecular weight but of a quite different ring structure due to the selective solubility of aromatic hydrocarbons. Table XVIII represents condensed data on the fractionation of a Pennsylvania neutral by distillation and solvent extraction [51, 1939].

Little can be said about the physical structure of lubricating oils; they are substantially homogeneous mixtures of hydrocarbons and other constituents, which are miscible in all proportions, with the exception of solid paraffins.

The theory of the colloid or 'isocolloid' structure of lubricating oils is frequently discussed and cited, in spite of its inherent improbability. The average molecular weight of lubricating oils varies from 350 to 800, i.e. much below that of colloids, which is of the order of at least 10,000. Even oxygen- and sulphur-containing neutral resins present in lubricating oils have a comparatively moderate molecular weight and form true non-colloidal solutions. Only asphaltenes form colloidal solutions in petroleum oils. The asphaltenes, however, are usually absent in lubricating oils, or may be present in some heavy, improperly refined lubricants in an amount not exceeding a small fraction of 1%.

TABLE XVIII

Fractionation of Filtered Pennsylvania Neutral by Distillation and Solvent Extraction

Cut no.	Wt. % of charge	Viscosity at 210° F.	Viscosity at 100° F.	Visc. index	Sp. gr. (20° C.)	Mol. weight	% of Arom. rings	% of Naph. rings	% of Paraffinic side chains	Aver. rings/mol.
Fractionation by Distillation										
Original	100	44·8	185·6	101	0·8713	407	9	15	76	1·70
1	2·84	36·3	78·5	92	0·8793	308	12	23	65	1·80
12	2·78	40·5	121·8	108	0·8653	360	8	15	77	1·50
24	2·46	47·2	229	96	0·8736	429	6	16	78	1·60
34	3·30	58·6	426	96	0·8779	512	9	14	77	2·00
Bottoms	6·07	72·5	700	95	0·8853	581	10	15	75	2·40
Fractionation by Reflux Extraction (Acetone)										
Original	100	44·8	185·6	101	0·8713	407	9	15	76	1·70
1	4·54	54·3	656	−37	0·9565	335	44	2	54	2·60
5	4·43	44·9	211	73	0·8930	353	17	17	66	2·05
10	4·29	41·3	128	115	0·8464	374	0	23	77	1·45
21	3·90	49·3	222	124	0·8496	473	0	16	84	1·25
Resid.	5·58	52·4	261	124	0·8523	506	0	15	85	1·30

Unsaturated and Aromatic Hydrocarbons.

In view of the absence of unsaturates in straight-run gasolines and gas oils, the presence of such hydrocarbons in lubricating oils seems improbable. The addition bromine numbers of lubricating fractions from various crudes are small, varying from 0·1–0·2 to 5·0. The highest addition numbers correspond to unstable high-boiling fractions of asphaltic crudes, which are appreciably decomposed at distillation temperatures. Thus it seems probable that the lubricating oils are completely saturated.

The content of aromatics in untreated lubricating-oil fractions varies from 10 to 40% by weight on the average. The above figures include also the content of neutral resins which contain oxygen and sulphur but have substantially a polycyclic aromatic structure. The content of aromatics in untreated lubricating distillates from Pennsylvania crude oils is close to 10% and in those from California crudes it amounts to 30%. The above figures of the content of aromatics were obtained by separation of aromatic hydrocarbons with sulphuric acid of proper concentration, which gives fairly reliable results.

The content of aromatic hydrocarbons (or aromatic rings) in an untreated lubricating oil is closely related to the commercial value of the stock. The aromatic hydrocarbons of lubricating stocks have a low viscosity index and are unstable towards oxidation, which transforms them into resinous and asphaltic products. Thus the content of aromatic hydrocarbons is an approximate measure of the undesirable constituents to be removed in the process of refining.

Little is known of the structure of aromatic hydrocarbons present in lubricating oils. This problem will be discussed later in the section on the rings of lubricating-oil hydrocarbons.

Paraffin Hydrocarbons. Paraffin hydrocarbons of normal or slightly branched structure, boiling in the range of lubricating oils, have high melting-points and are only slightly soluble in oils at low and moderate temperatures. The content of such hydrocarbons, composing petroleum wax, may be as high as 10% or more in lubricating distillates and residues from paraffin- and mixed-base crudes. In lubricating-oil distillates from naphthenic or asphaltic crudes the content of normal high-melting paraffins is usually very low, below 1%. The petroleum wax is separated from lubricating oils by filtration or centrifuging in suitable solvents. The commercial lubricating oils with low pour-points are practically free from normal and slightly branched paraffins of comparatively high melting-points.

Branched high molecular weight paraffins may have very low melting-points. Two factors determine the melting-point of a paraffin: the degree of branching and the position of the branch. Highly branched high molecular weight paraffins, i.e. with many branches, are liquid and have low melting-points. Moreover, a single branch in the molecule may have a quite different effect on the melting-point, depending upon its position: the central position of the side chain produces the maximum depressing effect, and vice versa. Thus, for example, all high molecular weight paraffins containing about 25 carbon atoms, which have one paraffinic side chain, C_4 or longer, in the middle of the molecule, are liquid at room temperature.

Such low melting-point isoparaffins are completely miscible with lubricating oils, and the presence of such isoparaffins in lubricating oils is at least not improbable.

Mair and Willingham [31, 1936] pointed out that none of the narrow wax-free lubricating fractions, produced from a Ponca City crude oil and treated with solvents, was observed to be richer in hydrogen than C_nH_{2n}, corresponding to monocyclic naphthenes. Any fraction consisting of bicyclic naphthenes and isoparaffins of the composition C_nH_{2n} should be easily separated by solvent treatment into a paraffinic raffinate and a naphthenic extract. Thus the authors came to the conclusion that 'no appreciable percentage of isoparaffins exists in these fractions'.

An extensive investigation along this line was made by Müller and Pilat [35, 1935]. Isoparaffins present in lubricating oils were separated by repeated extractions with various solvents. The final raffinate produced in a very small yield with respect to the original oil would contain at least a considerable proportion of isoparaffins, if those were present in the oil. A Polish bright stock (from Schodnica, sp. gr. 0·948 and molecular weight 535) was extracted 4 times with benzene-liquid sulphur dioxide, then 4 times with nitro benzene, then twice with furfural, and finally 24 times with pyridine. The last raffinate, obtained in a yield of 0·41% of the original oil, was not paraffinic, corresponding to $C_nH_{2n-0·8}$.

Three Pennsylvania lubricating oils of specific gravity 0·905 (molecular weight 657), 0·8748 (molecular weight 466), and 0·8685 (molecular weight 400) were treated with solvents in a similar manner. The final raffinate was crystallized in ethyl ether at −70° C. The crystallized raffinates were obtained in yields of 2·72, 1·2, and 7·5%, respectively, and had the following formulas: $C_nH_{2n-0\cdot4}$, $C_nH_{2n+0\cdot4}$, and $C_nH_{2n+0\cdot4}$. The last two raffinates may contain as much as 35% isoparaffins, if the naphthenes are monocyclic, or more, if they are not. Thus only the light Pennsylvania lubricating oil of specific gravity 0·8685 may contain as much as about 3% isoparaffins. In other Pennsylvania lubricating oils investigated, as well as in the naphthenic bright stock, the content of isoparaffins is negligible.

In addition to this, it should be pointed out that the fractions produced after the repeated extractions should contain also a certain proportion of normal paraffins which were not removed in the process of dewaxing. Therefore the content of isoparaffins should be correspondingly less. The pour-point of the raffinates $C_nH_{2n+0\cdot4}$ was above +10° C., indicating the possible presence of normal paraffins.

Thus it seems to be fairly safe to conclude that lubricating oils of low pour-point (produced directly from naphthenic crude oils or, after dewaxing, from paraffinic crude oils) are composed almost entirely of cyclic naphthenic and aromatic hydrocarbons, the percentage of isoparaffins in such oils either being negligible or not exceeding a few per cent. in some cases.

Paraffinic Side Chains. The length of paraffinic side chains in hydrocarbons of lubricating oils is calculated on the basis of molecular weight and the number of rings. For instance, Pennsylvania S.A.E. 20 and S.A.E. 40 (Table XVII) have long paraffinic side chains averaging C_{20} and C_{25} respectively, while California S.A.E. 20 and S.A.E. 40 have much shorter average paraffinic side chains C_{13} and C_{15} respectively.

As has been stated above, the viscosity index of lubricating oils is closely associated with the length of paraffinic side chains. Side chains of the order C_{20}—C_{25} make the viscosity index at least 100, those of the order C_{15} correspond to the viscosity index of about 50, and shorter side chains of from C_6 to C_7 are characteristic for lubricating oils with strongly negative viscosity indices.

Distribution of the paraffinic side chains in the cyclic molecules of lubricating oils is completely unknown. The number of carbon atoms in paraffinic side chains given above represents the average numbers which actually may be divided between two or more side chains.

Long paraffinic side chains are associated with naphthenic hydrocarbons, whereas the aromatic hydrocarbons present in lubricating oils usually have short ones. As a result the viscosity index of the aromatic portion of lubricating oils is low, and frequently negative. Thus any treatment of lubricating stocks removing aromatic hydrocarbons invariably increases the viscosity index of the treated products.

Very little is known of the structure of paraffinic side chains in lubricating oils. The occurrence of long normal paraffinic side chains (C_{15} or more) in lubricating oils of low pour-point seems improbable. The derivatives of benzene, cyclohexane, naphthalene, &c., with long normal paraffinic side chains (over C_{15}) have melting-points above 20° C. Such hydrocarbons, if present in original oils, would be removed with paraffin wax in the dewaxing operation. On the other hand, the corresponding derivatives of cyclic hydrocarbons with long branched paraffinic side chains may have very low melting-points. In addition to this, the division of a long paraffinic side chain into several shorter side chains may decrease enormously the melting-point. According to Mikeska, for instance, *n*-octodecylnaphthalene has a high melting-point (51–52° C.) whereas tri-*n*-hexylnaphthalene is liquid at room temperature [34*a*, 1936].

Thus it is probable that the cyclic hydrocarbons of lubricating oils with long paraffinic side chains have a branched chain structure or/and a side chain divided into a number of shorter chains.

Ring Structure. Very little is known of the structure of rings forming the cyclic hydrocarbons of lubricating oils. The analogy between low-boiling fractions and lubricating oils leads to the conclusion that the derivatives of benzene, cyclohexane, cyclopentane, naphthalene, hydrogenated naphthalenes, tricyclic aromatic, and hydro-aromatic hydrocarbons may be present in lubricating oils.

Davis and McAllister, Waterman *et al.* [43, 1945], and others showed that the average number of rings per molecule can be determined under certain assumptions. It corresponds to the average number of rings in cyclic molecules of low pour-point lubricating oils due to the fact that such oils consist almost entirely of cyclic hydrocarbons, as has been discussed above.

Tables 89, 90, and 92 give the data on the average number of rings in cyclic hydrocarbons of some lubricating oils, calculated by the Waterman method on the assumption that the rings are of the 6-carbon atom structure [43, 1945].

The most illuminating conclusions on the ring structure of lubricating oils were reported by Rossini [41, 1938], Leslie and Heuer [27, 1938], and Mair, Willingham and Streiff [32, 1938], as a result of extensive investigations of a lubricating stock from a Ponca City crude. The lubricating stock was produced from the crude in the amount of 10% and was dewaxed at −18° in ethylene chloride. The wax-free portion was subjected to extraction at 40° with liquid sulphur dioxide. The raffinate was treated with silica gel to produce a 'water-white' oil and a portion was adsorbed by silica gel. The extract in liquid sulphur dioxide was treated with petroleum ether at −55° to extract a 'petroleum-ether soluble' portion, an asphaltic portion remaining in the sulphur dioxide solution. The 'petroleum-ether soluble' portion was combined with the previous portion adsorbed by silica gel to produce the 'extract' portion of the lubricating stock. Thus the following fractions were separated:

1. The 'wax' portion, 35%.
2. The 'asphaltic' portion, 8%.
3. The 'extract' portion, 22%, boiling-range at 1 mm. from 170° to 290°, viscosity of fractions from 100 to 9,000 Saybolt units at 100° F., viscosity index from −80 to −150, density 0·98, refractive index 1·56, and specific dispersion 0·0195.
4. The 'water-white' portion, 35%, boiling-range at 1 mm. from 190° to 270°, viscosity of fractions from 100 to 500 Saybolt units at 100° F., viscosity index from 90 to 110, density (at 25°) from 0·86 to 0·89, refractive index (25°) from 1·47 to 1·49, specific dispersion 0·0102.

Only the 'water-white' and 'extract' portions were investigated. Both portions were fractionated by distillation and extraction. Each portion was first fractionated by distillation in high vacuum to produce a large number of substantially constant-boiling fractions. The fractions obtained were then fractionated by extraction to produce final 'homogeneous' fractions. Acetone (plus some water for more soluble fractions) was used as a solvent for the 'water-white' fractions and methyl cyanide (plus some acetone for less soluble fractions) for the 'extract' fractions. Each 'final' homogeneous fraction, representing 1/40,000 part of the original crude oil, consisted of compounds of substantially similar molecular size and type.

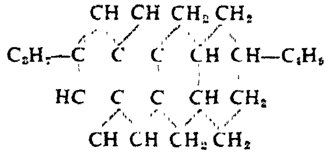
The fractions of the 'water-white' portion contained no sulphur, oxygen, or nitrogen, whereas those of the 'extract' portion contained, on the average, about 0·9 % sulphur, 0·1 % nitrogen, and 0·5 % oxygen.

The most important data for the following calculations and computations are: carbon content, hydrogen content, molecular weight, density, refractive index, specific dispersion, boiling-point, aniline point, and viscosities at 100° and 210° F. These data were determined for the 'water-white' and 'extract' portions. The latter were completely hydrogenated (until the specific dispersion reached 0·0100) and the same data were obtained for the hydrogenated fractions. The value of specific refraction or specific dispersion versus molecular weight will give important conclusions as to the number of aromatic and naphthenic rings in the molecule. For instance, the value of 0·0100 for specific dispersion shows that the hydrocarbons are purely naphthenic and that aromatic rings are absent. Another example: the value for specific dispersion of about 0·0130 for 20 carbon atoms shows that the hydrocarbons belong to the derivatives of either benzene or tetralin. The value of specific refraction for a certain number of carbon atoms depends upon the number of rings in the molecule. The increase in hydrogen content (or in the number of hydrogen atoms per molecule) after hydrogenation will give the number of aromatic rings in the virgin molecule before hydrogenation.

It has been postulated in all calculations that the naphthenic rings are of the 6-carbon type, and that the rings in aromatic and naphthenic hydrocarbons are condensed by joining through 2 carbon atoms. The most important results obtained concern the number of aromatic and naphthenic rings in molecules of lubricating oils from 1 to 4 *in toto*, and the combination of aromatic with naphthenic rings in one molecule. The aromatic rings, at least in lubricating oils of Mid-Continent origin, are combined with naphthenic-producing aromatic-naphthenic hydrocarbons which contain 1 naphthenic ring—1 aromatic ring (derivatives of tetralin), 2 naphthenic—1 aromatic, 3 naphthenic—1 aromatic, 2 naphthenic—2 aromatic, and 1 naphthenic—3 aromatic.

Another alternative—that the hydrocarbons in question consist of mixtures of aromatic and naphthenic hydrocarbons in suitable proportions—is ruled out. The aromatic and naphthenic hydrocarbons of the 'homogeneous' fractions would have different boiling-points and different solubilities in the solvent used, and would be easily separated in the operations of fractionation and solvent refining described above.

Rossini, for instance, gives the following formula for an 'extract' homogeneous fraction of specific gravity 1·004, molecular weight 334·5, and boiling-point 217° at 1 mm. of mercury:



As has been mentioned above, the 6-carbon atom structure of two naphthenic rings is arbitrary, as well as the position and distribution of the paraffinic side chain consisting of 7 carbon atoms. The average analysis of the lubricating stock is given in Table XIX.

Kurtz and Lipkin [24, 1940–1] made an attempt to determine the number of carbon atoms in the rings of lubricating-oil hydrocarbons on the basis of a relationship between the molecular volume of naphthenes and their ring structure. According to these calculations, half or more than half of the rings in some lubricating oils are of the 5-carbon atom (cyclopentane) type. If quantitative conclusions on the relative amount of 5- and 6-carbon atom rings in lubricating oils seem to be questionable, the importance of

TABLE XIX

Approximate Average Composition of a Lubricating Stock from Ponca City Crude with Respect to Rings of Molecules Containing from 20 to 40 Carbon Atoms

Part	*% of stock*	*Molecular composition*	*% in given portion*	*% in entire stock*
'Water-white' oil	35	1 naphth. ring+paraf. side chain 2 naph. rings+paraf. side chains 3 naphth. rings+paraf. side chains	92 {(15) (45) (32)}	32·2 {(5·3) (15·7) (11·2)}
		1 naphth. ring+1 arom. ring+paraf. side chains 2 naphth. rings+1 arom. ring+paraf. side chains	8	2·8
'Extract'	22	2 naphth. rings+paraf. side chains 3 naphth. rings+paraf. side chains	8	1·1
		2 naphth. rings+1 arom. ring+paraf. side chains 3 naphth. rings+1 arom. ring+paraf. side chains	25	5·5
		2 naphth. rings+2 arom. rings+paraf. side chains 1 naphth. ring+3 arom. rings+paraf. side chains	67 {(37) (30)}	14·7 {(8·1) (6·6)}
'Wax'	35	1, 2, or 3 naphth. rings+paraf. side chains. Normal paraffins+possibly some isoparaffins	50 to 25 50 to 75	17 to 9 18 to 26
'Asphalt'	8	Probably highly condensed aromatics together with the bulk of non-hydrocarbon material of the original fraction	..	..

the investigation of Kurtz and Lipkin remains in the proof that hydrocarbons composed of 5-carbon rings must be considered as normal constituents of lubricating oils. This finding evidently is in agreement with other data pertaining to the chemical composition of petroleum. The derivatives of cyclopentane are widely distributed in gasoline fractions. In addition to this, naphthenic acids of kerosines and gas oils have a ring structure of cyclopentane type. It is very probable that hydrocarbons of the cyclopentane type are present in gas oils and lubricating oils. The question of the possible presence of other cyclic structures than C_5 and C_6 rings in high-boiling oil fractions will be discussed separately for naphthenic and aromatic hydrocarbons.

It should be pointed out that lubricating-oil fractions, heavily treated with sulphuric acid or solvents and consisting of naphthenes, do not show optical exaltation and have the normal value of specific refraction. Grosse summarized the data on the optical exaltation of bicyclic and tricyclic naphthenes, and confirmed that polycyclic naphthenes containing five- and six-membered rings do not show optical exaltation, whereas those having four- and particularly three-membered rings invariably do. Thus it seems improbable that C_3 or C_4 cyclic naphthenes are present in lubricating oils in any combination with C_5 and C_6 ring structures.

The aromatic hydrocarbons of lubricating oils have high values of specific dispersion which, however, fall to the normal value of 99 after hydrogenation. This proves that the optical exaltation of lubricating-oil aromatics is due entirely to their aromatic structure. There are no C_3 or C_4 cyclic structures in the molecules of the aromatics; the latter, being unaffected by hydrogenation, would cause optical exaltation after hydrogenation.

The presence of C_7, C_8, &c., rings which do not display optical exaltation cannot be ruled out, but seems rather improbable in view of the absence of such hydrocarbons in gasolines. The six-membered and probably also five-membered rings should be considered as the basic ring structures of lubricating oils.

Optical rotation of heavy oil fractions, including lubricating oils, is apparently characteristic of polycyclic naphthenic structures, but the nature of the naphthenes responsible for this phenomenon is entirely unknown. Oils from naphthenic crudes are more active optically than those from paraffinic crudes. Treatment with sulphuric acid and removal of aromatic hydrocarbons does not appreciably affect the optical rotation. Callahan applied optical rotation to the identification of lubricating oils. The lubricating oils of Pennsylvania crudes have a value of rotation of less than +0·26. Higher values indicate a source other than that of Pennsylvania.

Individual Hydrocarbons of Lubricating Oils.

As has been pointed out, no individual hydrocarbons have so far been separated from lubricating fractions. Even the very narrow substantially constant-boiling 'final homogeneous' fractions isolated by the Bureau of Standards consisted of a series of hydrocarbons, however, of similar size and type. Each of these fractions represented only 0·0025% of the original Ponca City crude oil. It should be remembered that the hydrocarbons separated from lighter-boiling fractions (gasoline and kerosine) represented from 1·5 to 0·02% of the original crude. This comparison shows that any individual hydrocarbon is present in lubricating oils in a much smaller percentage than in gasoline and kerosine fractions, obviously because of the tremendous number of possible isomers. The narrow fractions, representing 0·0025% of the crude, would consist of a single pure hydrocarbon for low-boiling fractions and of numerous hydrocarbons for lubricating oils.

In addition to this, the properties (boiling-point, melting-point, solubility, &c.) of high molecular weight hydrocarbons of approximately the same size may be very similar. As a result, the problem of separating individual hydrocarbons from lubricating oils is extremely difficult and is far from the solution.

The difference in the complexity of the composition of gasolines and lubricating oils may be illustrated by the following comparison. As stated earlier, over 75% of the light Ponca City gasoline (55–145° C.) has been assigned to approximately 40 hydrocarbons. The total number of hydrocarbons composing the light gasoline will be appreciably greater than this, since the remaining 25% of the gasoline consists of hydrocarbons, each of which is represented by a comparatively small percentage. Assuming the average percentage of the unseparated hydrocarbons to be 0·02 of the crude or 0·15 of the gasoline (the minimum percentage in the hydrocarbons separated), the number of unseparated hydrocarbons will be 165 and the total number of hydrocarbons in the gasoline close to 200. In any case, the total number of hydrocarbons constituting the gasoline cannot be excessive, except perhaps those present in very minute amounts.

The 'final homogeneous' fractions of the lubricating stock produced by the Bureau of Standards constitute 1/40,000 part of the crude or 1/4,000 of the lubricating stock. The number of individual hydrocarbons in each fraction is unknown and can be assumed equal to the average value *n*, which should be much greater than 1. Thus the total number of hydrocarbons in the lubricating stock would be 4,000*n*, and would show the complexity of lubricating oils as compared with gasolines.

Petroleum Wax

Types of Petroleum Wax.

Petroleum wax represents solid hydrocarbons, mostly paraffinic, which occur in crude oils, distillates, and residues, and have a 'waxy' structure and melting-points above 30–35° (86–95° F.). The last limitation, however arbitrary, appears to be substantial, since the paraffins of lower melting-points, largely represented in gas-oil fractions, are not considered as petroleum wax. Such hydrocarbons are readily dissolved in petroleum fractions even at low temperatures, and cannot be separated by the conventional methods used in the manufacture of petroleum wax. Paraffin wax and other petroleum waxes are produced from comparatively high-boiling fractions, such as heavier gas oils, paraffin distillates, and residues. It is understood that the borderline between 'solid' petroleum wax hydrocarbons and 'liquid' paraffins is neither definite nor scientific. Normal eicosane with a melting-point of 36·4° C. is rather close to this borderline.

Highly cracked products may contain such solid hydrocarbons as naphthalene or derivatives of anthracene or phenanthrene, which do not have a waxy structure and thus do not belong to the petroleum waxes. As will be seen later, some petroleum waxes probably have a ring structure, but in any case they possess long paraffinic side chains which are closely related to the so-called waxy structure.

The nomenclature of petroleum waxes is not definite.

The name 'paraffin wax' is sometimes used as a generic term embracing all solid paraffins and similar hydrocarbons of waxy structure, which are present in crude oils and distillates. The generic term 'petroleum wax' used in this article is preferable. The former term is used in a more specific sense to designate the petroleum wax separated or manufactured from comparatively light petroleum fractions, including gas oil and neutrals. Petroleum ceresin or microcrystalline wax is that separated from residues or petrolatum. Rod wax is formed by spontaneous precipitation from crude oils in sucker rods or in storage; it contains high molecular weight petroleum waxes of the ceresin type.

The properties of paraffin wax and petroleum ceresin are quite different. Paraffin wax crystallizes in large crystals, plates, or needles. It absorbs loosely the oils which can be easily separated by filtration or sweating under appropriate conditions. Petroleum ceresin crystallizes in such small crystals that the earlier investigators attributed an amorphous structure to it. Detection of the crystalline structure in petroleum ceresin under a microscope does not present any difficulties, however. Microcrystalline wax absorbs or adsorbs oils tenaciously, the separation of which is a much more difficult problem than in the case of paraffin wax.

The properties of paraffin wax, which consists mostly of normal paraffins, as will be seen later, are uniform and do not depend on the origin. Thus oil-free paraffin waxes, produced from any crude oil, will have the same properties. There is no evidence that the same would be true of petroleum ceresins; it is quite possible that petroleum ceresins of the same melting-point will differ to a certain extent in their properties, depending upon their origin and structure.

Content of Petroleum Wax in Crude Oils.

The content of petroleum wax in crude oils varies within broad limits. The wax content of naphthenic and asphaltic crude oils is usually small, not exceeding 1%, but may be comparatively high in some crudes of these types. Paraffin-base and mixed-base crude oils may contain as much as 10% of petroleum wax. Table XX gives some data on the petroleum wax content in various crude oils. It should be kept in mind that the figures given in the table have been obtained by different methods and in various laboratories. In some cases the Holde–Engler method with destructive distillation, resulting in a partial cracking of petroleum wax, was employed. Thus the data are not quite comparable and in some cases may be appreciably lower than the actual percentage of petroleum wax.

TABLE XX

Content of Petroleum Wax in Various Crude Oils

Origin of crude oil	*Sp. gr. 60/60° F.*	% of petroleum wax
United States		
Pennsylvania, average	0·805	2·4
Oklahoma, Tonkawa	0·810	2·1
Oklahoma, Oklahoma City	0·832	4·0
East Texas, Longview	0·831	7·0
West Texas, Pecos	0·852	0·25
Texas, Panhandle	0·810	6·0
Arkansas, Smackover	0·918	2·1
Gulf Coast, Placedo	0·905	0·4
Louisiana, Rodessa	0·810	5·2
California, Sante Fe Springs	0·865	1·5
California, Huntington Beach	0·897	1·9
California, Midway	0·934	0·6
Other countries		
Mexico, Poza Rica	0·873	3·9
Mexico, Panuco	0·988	0·55
Venezuela, La Conception	0·850	3·6
Venezuela, La Rosa	0·910	0·7
Venezuela, Lagunillas	0·950	0·35
Russia, Surachany (Baku)	0·860	2·5; 6·0*
Russia, Balachany (Baku)	0·867	0·5; 2·0*
Russia, Bibi-Eibat (Baku)	0·865	0·4; 1·3*
Russia, Emba-Dossor	0·859	0·3
Russia, Grozny (Waxy)	0·838	6·5; 8·5*
Russia, Grozny	0·875	0·3
Russia, Maikop	0·830	0·5
Roumania, Moreni	0·795	4·8
Roumania, Bustenari	0·835	0·45
Iraq, Kirkuk	0·844	1·9
Iran, Maidan-i-Naftun	0·837	4·5
Burma	0·835	8·0
Assam	0·856	10·7

* The first figure of the wax content has been obtained by the destructive distillation method and the second figure without the distillation.

Straight-run distillation of paraffin-base and mixed-base crude oils gives paraffin distillates usually boiling from 150° (302° F.) to 300° (572° F.) at 10 mm. pressure and containing from 10 to 25% of paraffin waxes, including those of low melting-point. The slack wax, obtained by filtration of chilled paraffin distillate (eventually in a solvent), contains 60% or more of paraffin wax. The scale wax is obtained from the slack wax by sweating or by crystallization from a solvent and contains upwards of 97% of paraffin wax.

Straight-run or 'steam-refined' residues (long residues or cylinder stocks) of paraffin-base or mixed-base crude oils contain 10 to 25% of petroleum wax. In the process of dewaxing this is removed in petrolatum, which may contain from 25 to 40% of petroleum wax. The separation of petroleum wax from petrolatum by crystallization in a solvent and filtration produces the so-called petroleum ceresin, which differs substantially from paraffin wax and somewhat resembles the ceresin obtainable from ozokerite. The content of microcrystalline wax or ceresin in commerical products may vary from 80 to 95%, depending upon the conditions of crystallization.

The content of petroleum wax in raw rod wax varies from 50 to 70%, the remainder being oils and asphaltic-resinous substances. The melting-point of purified rod waxes is from 55 to 82° C. (130 to 180° F.) (Reistle and Blade [40, 1932]).

Normal Paraffins in Petroleum Waxes.

The question of the chemical structure of petroleum waxes is comparatively old. Załoziecky made a distinction between distilled crystalline paraffin wax consisting of normal paraffin hydrocarbons and the virgin amorphous petroleum wax made up of isoparaffins. The amorphous isoparaffins of crude oils are transformed into crystalline normal paraffins by cracking or splitting of side chains, which takes place on distillation.

Gurwitch [17, 1934] was the first to show that there is no essential difference in the crystalline structure of distilled and virgin petroleum waxes. The virgin 'amorphous' petroleum wax is in reality crystalline, but the size of the crystals is much less than in the case of distilled paraffin waxes. Sachanen and Bestougeff [44, 1926] showed further that virgin petroleum waxes, separated directly from a crude oil, dissolve in oils and organic solvents, forming saturated solutions. Their solubility changes with temperature in the same manner as that of distilled paraffin waxes and other crystalline substances.

On the other hand, Zaloziecky's assumption that distilled paraffin waxes are normal paraffins has been proved to be correct, at least to a great extent. As will be seen later, commercial paraffin waxes are predominantly normal paraffins. Isoparaffins are also present in distilled paraffin waxes and particularly in residues.

The proofs that the commercial paraffin waxes consist mostly of normal paraffins are numerous and convincing. First, Kraft [23, 1888, 1907] showed that the narrow fractions of paraffin wax from a brown coal tar had the same properties as the individual normal paraffins synthesized by this experimenter. The data of Francis *et al.* [13, 1922] also show that the hydrocarbons of shale paraffin wax correspond more or less to normal paraffins. Mabery [28, 1905] fractionated a commercial paraffin wax and separated paraffins from $C_{23}H_{48}$ to $C_{29}H_{60}$, the melting-points of which corresponded to those of normal paraffins.

Carpenter [6, 1926] studied the fractions obtained from Burma petroleum waxes. The melting-point of the fractions varied from 41 to 71·7° C. The waxes consisted of a series of paraffins from $C_{21}H_{44}$ to $C_{34}H_{70}$. Higher molecular weight hydrocarbons were obtained from sucker rod-wax from the same crude oil. The properties of the fractions corresponded closely to those of normal paraffins. However, some anomalies in the molecular weight in the case of 66·5° C. and 70·0° C. waxes suggested the possibility of the presence of isomeric paraffins.

Buchler and Graves [4, 1927] studied the narrow fractions of the waxes produced from paraffin wax, slop wax, petrolatum wax, and rod wax of Salt Creek crude oil (Wyoming). Each wax was recrystallized from ethene chloride at 40° F. until one of constant melting-point and refractive index was obtained. The oil-free wax was then fractionated under a pressure of less than 1 mm. of mercury. Thus each of the four waxes was resolved into a series of narrow fractions, whose melting-points and refractive indices (at 84° C.) were determined. When the values of refractive index were plotted against the melting-points, it was shown that the refractive indices of the lower fractions fell approximately on a straight line, whereas those of the higher fractions (melting-points above 55° C.) were markedly higher. The authors believed that this discrepancy was due to the presence of some unknown impurity which was removed by hot crystallization at 35–40° C. in ethene dichloride. In this way a very small amount of 'waxy impurity' or 'soft wax' was obtained. The refractive index of the fractions purified by this method, and plotted versus melting-point gave a straight line. The physical properties of the purified fractions were very close to those of synthetic normal paraffins. The authors concluded that petroleum waxes consist of straight-chain paraffins and an admixture of 'soft wax', which affects the crystallization of paraffins.

It should be pointed out that repeated crystallization and separation of petroleum waxes ('until a wax of constant melting point and refractive index was obtained') and further crystallization in hot solvent will remove completely all isoparaffins which are of lower melting-point and higher solubility in solvents. Thus it is not surprising that the purified petroleum waxes turned out to be normal paraffins. Neither the petroleum waxes removed by crystallization nor the 'soft wax' were investigated by the authors, who, for this reason, failed to show the presence of branched paraffins in petroleum waxes.

The normal structure of the paraffins composing commercial paraffin waxes should not be understood too literally. The 'terminal' isoparaffins with short side chains, e.g. isoparaffins with one methyl group in position 2, do not differ appreciably in their physical properties from normal paraffins of the same molecular weight. The melting-point of such isoparaffins in paraffin waxes would be 5 to 10° C. lower, and their solubility in various solvents correspondingly greater as compared with normal paraffins of the same number of carbon atoms. The specific gravity and refractive index would be close to those of normal paraffins. Therefore the presence in paraffin wax of such terminal isoparaffins with short side chains cannot be ruled out.

The action of fuming sulphuric acid or chlorosulphonic acid on the isoparaffins in question is unknown. If these reagents react with the terminal isoparaffins in the same manner as with other branched paraffins (see the next section), the reaction may be used for the clarification of this problem, as well as other appropriate methods, including the X-ray and infra-red ray methods.

Sachanen and Tilicheyev [45, 1929] showed that the cracking of commercial paraffin wax yields hydrocarbons of normal structure. A commercial paraffin wax, melting-point 57–58° C., was found on fractionation to consist mostly of $C_{24}H_{50}$ to $C_{26}H_{54}$ paraffins. Cracking under moderate temperature–time conditions gave liquid products which were then fractionated, treated with sulphuric acid, and redistilled to remove unsaturated hydrocarbons. The treated fractions were highly paraffinic and contained about 10% of naphthenes. Recrystallization of the fractions produced pure normal paraffins of various molecular weights up to $C_{17}H_{36}$. Thus normal paraffins are formed as a result of cracking $C_{24}H_{50}$—$C_{26}H_{56}$ hydrocarbons of commercial paraffin wax.

It can be stated on the basis of the above studies that commercial paraffin waxes are mixtures mostly of normal paraffins from $C_{22}H_{46}$ to $C_{30}H_{62}$, the proportion of which depends upon the melting-point of the wax. Normal hydrocarbons of higher molecular weights can be separated from such wax products as petrolatum wax, rod wax, &c. The separation of normal paraffins from these waxes, however, is more difficult in view of the presence of isoparaffins, as will be shown later.

Isoparaffins in Petroleum Waxes.

Ferris, Cowles, and Henderson [10, 1929, 1931] investigated narrow fractions of a paraffin wax from a Mid-Continent crude oil. These were separated by fractionation of oil-free waxes at an absolute pressure of less than 1 mm. of mercury in a 5-foot column. The fractions obtained had boiling-ranges of approximately 15° C. The oil-free waxes were obtained separately from scale wax, slack wax, foots oil, and sweat oil by successive crystallization from ethane dichloride at −18° C. The fractions having identical 50% boiling-points or refractive indices varied widely in melting-point, particularly the high-boiling (or high refractive index) ones. The fractions produced from scale wax had higher melting-points than those produced from slack wax, &c.; those from sweat oil had the lowest melting-points. By systematic crystallization of two fractions of about the same boiling-range six more uniform fractions having practically the same molecular weight and boiling-range were obtained, whereas their other properties, such as melting-point, specific gravity, &c., were quite different. The melting-point varied from 59·9° C. to 29·4° C. and the specific gravity from 0·770 to 0·792 correspondingly for the wax fractions of the identical molecular weight of about 270.

The data obtained cannot be explained on the assumption that waxes of the same boiling-range consist of various mixtures of saturated straight-chain hydrocarbons with the 'soft' wax. The authors believe that paraffin wax contains not only straight-chain paraffins but also various types of branched paraffins which have lower melting-points, higher specific gravities and refractive indices, and greater solubility. The agreement between calculated (on the basis of C_nH_{2n+2}) and observed values of molecular refraction shows that all hydrocarbons are paraffins.

Clark and Smith [7, 1931] studied the X-ray diffraction of the fractions investigated by Ferris *et al.* and verified in general the conclusions of these authors.

Yannaquis [52, 1934, 1938] obtained similar results, having fractionated paraffin waxes by extraction in benzene. The most soluble fractions contained isoparaffins, whereas the least soluble fractions and the residuum consisted predominantly of normal paraffins. Infra-red rays were used in this investigation.

Normal paraffins predominate in petroleum waxes from Mid-Continent crudes, particularly in paraffin waxes. According to Sachanen, Wassilieff, and Sherdeva [47, 1931] there are crude oils in which the petroleum waxes are chiefly isoparaffins. These authors studied the narrow fractions of petroleum waxes from two Russian crude oils from the Grozny and Surachany oilfields. The fractions were obtained by crystallization in ethene dichloride and distillation under high vacuum. The molecular weight, specific gravity, melting-point, and viscosity, as well as the ultimate analysis, were determined for each fraction. The elemental composition and formulas correspond closely to hydrocarbons of the series C_nH_{2n+2}. The melting-points of the Grozny petroleum waxes correspond closely to those of normal paraffins, whereas the melting-points of Surachany petroleum waxes lie as much as 20° C. lower than those of normal paraffins at the same molecular weight. The specific gravities of Grozny petroleum waxes also coincide with the curve for normal paraffins, whereas those of Surachany waxes are much higher than those of normal paraffin at the same molecular weight.

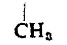
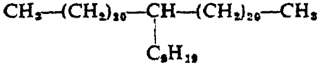
Kolvoort, Moser, and Verver [22, 1937] fractionated petroleum waxes from Rangoon, Java, and Roumania crude oils. The wax fractions of the Java crude oil correspond to normal paraffins, with the exception of the last fractions. Only the first fractions of the Roumania petroleum wax correspond to normal paraffins. The higher wax fractions of both crude oils have lower melting-points and higher specific gravities and are probably isoparaffins. Thus Borneo, Java, and Rangoon crude oils are rich in normal paraffins, whereas Roumania crude oil is richer in isoparaffins. The proportion of isoparaffins in the latter, however, is apparently much lower than in the Surachany crudes.

It should be pointed out that the specific gravity of isoparaffins isolated from the Surachany crude oil, of molecular weight C_{37} to C_{53}, changes rather irregularly in the range from 0·782 to 0·787. In any case there is no gradual increase of specific gravity with increasing molecular weight, as takes place with normal paraffins or wax fractions corresponding to normal paraffins. This peculiarity of Surachany isoparaffins is evidently related to their isostructure. It is hardly to be expected that the isoparaffins of petroleum waxes would belong to the same homologous series. It seems more probable that the iso-structure of such isoparaffins will vary from fraction to fraction causing irregularity in the change of specific gravity or refractive index with increasing molecular weight. It should be remembered that the isoparaffins of gasoline fractions also belong to various classes, beginning with slightly branched and ending with highly branched hydrocarbons.

The structure and the degree of branching of isoparaffins from petroleum waxes is unknown. The melting-points of isoparaffins separated from Mid-Continent and Surachany crude oils is on the average 20° C. lower than that of normal paraffins at the same molecular weight. Such a comparatively small difference indicates that the degree of branching of the isoparaffins in question is also comparatively small. According to the data systematized by Egloff [9, 1940], the difference in the melting-point of normal high molecular weight paraffins (C_{28} or more) and those with one or two methyl groups in side chains is from 10° to 30° C. Thus it is probable that the solid isoparaffins of petroleum waxes are slightly branched, for instance, with one or two methyl groups in the side chains. It is interesting to remember that such structures are quite common in low-boiling oil fractions, e.g. in gasolines and naphthas.

Pogacnick [39, 1932] came to the same conclusion on comparing the properties of ceresin fractions and of synthesized isoparaffins. The ceresins are similar to the synthetic isoparaffins with short side chains (methyl and ethyl groups) in the middle of the main chain.

Recent investigations have amplified our knowledge of the branched paraffins and verified the above conclusions. Backer and Strating [2, 1940] synthesized some high molecular weight normal and branched paraffins and found that the branching in the middle of the molecule strongly affects the melting-point, as the following data clearly show:

Hydrocarbon	*Melting-point (° C.)*
Normal tritetracontane, $C_{43}H_{88}$ $CH_3—(CH_2)_{41}—CH_3$	85
Methyl-di-heneicosyl-methane, $C_{44}H_{90}$  $CH_3—(CH_2)_{20}—\underset{\displaystyle CH_3}{\underset{\vert}{CH}}—(CH_2)_{20}—CH_3$	66·6–61·7 (two modifications)
Nonyl-di-heneicosyl-methane, $C_{52}H_{104}$  $CH_3—(CH_2)_{20}—\underset{\displaystyle C_9H_{19}}{\underset{\vert}{CH}}—(CH_2)_{20}—CH_3$	32·7–39·0

Thus the replacement of a hydrogen atom in the middle of a high molecular weight and high melting-point normal paraffin with a methyl group results in the lowering of the melting-point approximately 20° C. and with a nonyl group 45° C.

The data by Cosby and Sutherland [8, 1941] show that the difference in the melting-point of *n*-butyldocosanes is as high as 20·8° C. by shifting the butyl group from position 5 to position 11. The melting-point of normal hexacosane (57° C.) drops to 0° C. by one butyl branching in the middle of the molecule.

Another proof of the branching of petroleum isoparaffins in the middle or central parts of the molecules is a higher specific gravity (or refractive index) as compared with normal paraffins. The specific gravity and refractive index are higher for isomers with side chains in the middle of the molecule, whereas side chains at the ends cause a decrease in the values of these properties as compared with the normal hydrocarbon.

The viscosity of petroleum waxes supposed to be rich in isoparaffins also indicates the iso-structure of these hydrocarbons, as well as the central branching of molecules. Sachanen, Wassilieff, and Sherdeva [47, 1931] determined the viscosity of some Grozny and Surachany petroleum-wax fractions at 80° to 100° C. The waxes or isoparaffins of Surachany crude oil are much more viscous than the waxes or normal paraffins of Grozny crude oil at the same molecular weight. The viscosity of isoparaffins branched close to the ends of the molecule is lower than that of normal paraffins of the same molecular weight, whereas the viscosity of isoparaffins branched in the middle, particularly with two side chains, is greater than that of normal hydrocarbons. Thus the viscosity of petroleum ceresins is another proof of their iso-structure and branching in the central parts of the molecules.

Chemical data on the petroleum waxes are also in accordance with the above conclusions. It is known that isoparaffins are much more susceptible to oxidation reactions than normal paraffins. They react, for instance, with fuming sulphuric or chlorosulphonic acid, whereas normal paraffins are almost inert with respect to these reagents. Accordingly, ceresin from ozokerite reacts with fuming sulphuric or chlorosulphonic acid, whereas paraffin wax is almost inert to these reagents. Holde and Schunemann [19, 1928] suggested using this difference in the behaviour of paraffin waxes and ceresins towards fuming sulphuric acid for the evaluation of the content of paraffin wax in commercial ceresins. Sachanen and Sherdeva found that petroleum waxes separated from Surachany crude oil and consisting of isoparaffins are readily attacked by fuming sulphuric or chlorosulphonic acid. For instance, the treatment of a Surachany ceresin, melting-point 84° C., with 800% by weight of fuming sulphuric acid at 100° C., decomposed 25·4% of the ceresin, while under the same conditions a Grozny paraffin wax was practically undecomposed (0·9% loss). With a greater excess of fuming sulphuric acid (35 times with respect to the wax), the decomposition of Surachany waxes was as high as 49·3 to 76·6%.

An interesting application of the nitration method to commercial paraffin wax and Surachany ceresin has been made by Nametkin and Nifontova [36, 1934, 1936]. These authors nitrated commercial paraffin waxes by Konovalov's method and found that the nitro compounds formed were mostly soluble in alcoholic sodium hydroxide, indicating normal hydrocarbon structure. Nitration of a Surachany ceresin (melting point 87·7° C.) gave quite different results. A 'nitroceresin' insoluble in alkali was formed as a main product (yield 53%), whereas the yield of the impure 'nitroparaffins' of normal structure was only 10·7%.

Zaloziecky's assumption that virgin isoparaffins are transformed into normal paraffins on distillation cannot be accepted in this general form. Isoparaffins from C_{25} to C_{45} can be distilled with negligible decomposition and without being converted to normal paraffins. Sachanen, Wassilieff, and Sherdeva [47, 1931] distilled in cathodic vacuum ceresin waxes consisting of isoparaffins C_{25} to C_{45}, without cracking and transformation to normal hydrocarbons. On the other hand, high molecular weight isoparaffins distilled at atmospheric pressure are partially decomposed and give normal paraffins, as proved by Suida and Planckh [48, 1933]. The isoparaffins 16-methylhentriacontane (melting-point 34° C.) and 16-butylhentriacontane (melting-point 23° C.) were distilled at atmospheric pressure. The distillates formed were recrystallized from glacial acetic acid and gave a paraffin of melting-point 68–69° C. in the first case and one of melting-point 62–63° C. in the second case. Thus the distillation at atmospheric pressure of heavy residues containing isoparaffins of high molecular weight may be accompanied by a partial decomposition of the isoparaffins with formation of normal hydrocarbons.

It may be concluded on the basis of the foregoing discussion that the isoparaffinic structure of the so-called petroleum ceresins has been established firmly. It is understood, however, that commercial petroleum ceresins may contain a variable proportion of normal paraffins. In many cases this proportion may be fairly high, due to the fact that isoparaffins, even in a moderate proportion, impose their crystalline structure and properties on normal paraffins.

Cyclic Hydrocarbons in Petroleum Waxes.

McKittrick, Henriques, and Wolff [34, 1937] made an extensive study of the petroleum waxes separated from distillates, residues, and petrolata of various crude oils. Each petroleum wax was fractionated from ethene dichloride or chloroform. Various fractions were obtained, the last having been produced at −35° C. from ethene dichloride and at −55° C. from chloroform. The melting-points and refractive indices were determined for each fraction. The original paper presents the curves of refractive index versus molecular weight for each wax; these are compared with corresponding curves for hydrocarbons, including normal paraffins, isoparaffins, naphthenes, and aromatics. In one case for Parawax (commercial paraffin wax of the Standard Oil Co. of New Jersey, melting-point 51·5° C.) the separated fractions (melting-points from 37° to 64° C.) gave refractive indices which practically correspond to normal paraffins of the same melting-point, the result being in complete accord with the previous conclusions of the preceding sections.

In other cases the curves of refractive index versus melting-point are above the curve for normal paraffins and in some cases above that for isoparaffins, indicating the presence of cyclic hydrocarbons. The curves for distillate waxes lie nearly parallel and fairly close to the line for normal paraffins in the region of higher melting-points. The portion of the curves in the region of lower melting-points rises above the normal paraffin line and enters into the region of naphthenes. The authors conclude that the higher-melting fractions of distillate waxes are predominantly normal paraffins, and that the lower-melting fractions, as well as the waxes of residues and petrolata, are rich in naphthenes and aromatics.

These conclusions, however, do not seem to be convincing. The data on the purity of the fractions produced and the ultimate analyses are lacking. As a matter of fact, the abnormally high values of refractive index of the fractions may be due to the impurities or to the presence of naphthenic and aromatic hydrocarbons. It is significant that the greatest deviations from the lines of paraffins were observed for low-melting waxes (20° to 40° C.). These fractions were obtained at very low temperatures of crystallization, from −35° to −55° C., and might be particularly impure.

The earlier data of Müller and Pilat [35, 1935] on the presence of cyclic paraffin waxes appear to be more convincing. They found that petroleum waxes separated from asphalts have a chemical composition corresponding to the formula C_nH_{2n-m}. A sample of asphalt from a Boryslav crude oil was shaken with an excess of petroleum ether. The petroleum wax obtained after evaporation of the ether was crystallized twice from pyridine. Further refining was carried out by decolorization with charcoal in hot benzene and by subsequent crystallization from ether. By fractionation from benzene the wax was separated into four portions with melting-points from 49–56° to 75–80·5° C. and molecular weights from 695 to 775. The iodine numbers ranged from 1·4 to 4·1. The formulae of the fractions corresponded to $C_nH_{2n-0·8}$ to $C_nH_{2n-3·1}$, indicating cyclic structure. The specific gravities and refractive indices of the fractions were appreciably higher than those of the corresponding paraffins.

Another petroleum wax was separated from a Boryslav crude oil by fractionation with methane at low temperatures and by precipitation of the asphalt-free residuum with alcohol. The wax precipitated was crystallized from pyridine-alcohol, then from acetone-benzene, and finally from ether. The second fraction, more soluble in ether, had the formula $C_{33·2}H_{67·2}$, corresponding to $C_nH_{2n-0·8}$.

The authors believe that the wax fractions produced consisted entirely of waxes due to numerous fractionations. If so, the appreciable deviations from the formula C_nH_{2n+2} are significant and may be considered as a proof of the cyclic structure of these hydrocarbons.

Yannaquis [52, 1934, 1938] studied a commercial paraffin wax of Pechelbronne and its fractions (melting-points from 45·1–56·5° to 64·7–67·9° C.) by X-rays and in a microscope in polarized light. He found that the waxes have two crystalline forms, one of which is due to paraffins and the other to cyclic hydrocarbons.

Mair and Schicktanz [30, 1936] performed a series of combustion analyses of three wax samples, obtained by Ferris and his co-workers, with an accuracy of approximately ±0·0005 for the ratio of hydrogen to carbon. The samples contained a small proportion of some oxygen compounds. Corrections were calculated on the assumption that the oxygen was present in an aldehyde or ketone form. Whereas the high-melting fraction (melting-point 65·5° C. and molecular weight 420·5) corresponded to the formula C_nH_{2n+2}, the two low-melting fractions of about the same boiling-range and molecular weight (melting-points 38·8 and 34·0° C., respectively) had the formulas $C_nH_{2n+0·67}$ and $C_nH_{2n+0·51}$, respectively. The authors concluded that these wax fractions were composed of about 70 and 75% of molecules of the series C_nH_{2n}, i.e. of monocyclic structure, or of correspondingly smaller amounts of molecules of polycyclic hydrocarbons. Thus it is not improbable that the so-called isoparaffins may contain a certain proportion of cyclic hydrocarbons.

As a result of studies referred to in these sections, a general conclusion should be drawn that the petroleum waxes consist predominantly of paraffin hydrocarbons. Normal paraffins predominate in commercial paraffin waxes because isoparaffins of the same boiling-range are more soluble in oils and are separated in the operations of crystallization and sweating. Branched isoparaffins of lower melting-point and higher solubility are present in all distilled fractions containing petroleum waxes. In general, the high-boiling fractions and residues contain a larger proportion of branched paraffins. The nature of the crude oils is another factor affecting the proportion of branched paraffins. There are some crudes which are particularly rich in branched solid paraffins, as, for example, Surachany. The petroleum waxes of most paraffin and mixed-base crudes, however, consist chiefly of normal paraffins.

The isoparaffins of petroleum waxes probably belong to comparatively slightly branched isoparaffins with branches in the middle or in the central parts of their molecules. The presence of cyclic petroleum waxes, i.e. solid waxy hydrocarbons of cyclic structure with long paraffinic side chains, has not been definitely proved, but seems probable.

Classification of Crude Oils

Geological Identification of Crude Oils.

From the geological standpoint, the crude oils are identified by productive sands, sandstones, and limestones. It is reasonable to expect that a given oil-bearing sand would contain a reasonably uniform crude oil, that is to say, of uniform chemical and fractional composition. Some minor deviations from the average, however, are possible, due, for example, to the changing gas factor; to the local factors affecting the saturation of the crude oil with gas; to the adsorption effect of clay beds, &c. May, Miners, and Spinks [33, 1943] studied the crude oils produced from six wells of the Turner Valley oilfield (Lower Cretaceous) in an area of about 50 square miles. The refractive index of narrow fractions versus the boiling-range gives about the same curve for all six crudes, with minor deviations. Hendrickson, Hutcheon, and Spinks [18, 1942] determined the content of benzene, toluene, and xylenes plus ethylbenzene in the above crude oils and found that benzene varied from 0·33 to 0·63%, toluene from 1·34 to 2·05%, and xylenes plus ethylbenzene from 1·71 to 2·05%. These deviations may be considered as comparatively small, considering the difficulties involved in the separation of narrow fractions and the analytical determination of hydrocarbons.

In many cases the fractional and chemical compositions of crude oil from the same producing sand are identical or almost identical in fairly distant pools. For instance, the most prolific Woodbine sand (Cretaceous) in the East Texas field produces crudes which are practically identical, varying in the narrow range of specific gravity from 0·825 to 0·835 and of sulphur content from 0·25 to 0·40%, the other properties also being very similar. Moreover, the Woodbine crude oils from other oilfields close to the East Texas field differ from the above type to only a small extent: the Van Zandt crude from the same sand (60 miles to west) has a somewhat higher specific gravity (about 0·865) and a higher sulphur content (0·90%); the Haynesville crude (Woodbine sand, 100 miles to east) has specific gravity 0·845 and sulphur content 0·30%; the other properties of the two crudes are very similar to those of the East Texas field.

The Ordovician Wilcox sand produces practically identical crude oils in the fields of Oklahoma City, Marshall, Tonkawa, Okmulgee, and Ponca City (specific gravity 0·830 and sulphur content 0·2%), while the crudes from the same sand in Seminole and Yale are of somewhat higher specific gravity and sulphur content, being, however, very similar to the crude oil mentioned above.

In other cases, oilfields which are close together may produce quite different crudes from the same stratum. The crude oils of two Grozny oilfields, the New and Old, are produced from the same Tertiary sands, easily identified by Spaniodontella and Spirialis (Middle Miocene). Notwithstanding the close proximity of the two oilfields (about 10 miles) the crudes are quite different—highly paraffinic in the New Grozny field and highly naphthenic or asphaltic in the Old Grozny field. The Baku oilfields, distributed on the small area of the Apsheron peninsula, have a series of productive strata in Pliocene and Upper and Middle

Miocene, which may produce quite different crudes from the same sand in different pools.

Different oil-bearing sands of the same pool may produce similar as well as quite different crudes. The productive strata of the Pennsylvania fields are in the range of Devonian to Pennsylvanian formations (Carboniferous), and commonly produce crude oils which are very similar in respect to chemical and fractional composition.

On the contrary, the Russian oilfields, with many producing sands, may give quite varied crude oils in different sands of the same pool. As mentioned above, the Baku oilfields have numerous productive Pliocene and Miocene strata, e.g. as many as thirty-five oil-bearing sands in the Balachany-Sabunchy field. Some of the sands in the same pool yield quite similar crudes, whereas in other sands the properties of the crudes may change more or less gradually from stratum to stratum. The Old Grozny field is similar to the Baku fields and produces at least three different types of crude in its sixteen producing sands. The New Grozny field has twenty-four producing sands, all of which yield almost identical crudes with a high content of paraffin wax.

Thus geological identification of crude oils requires identification of both the oilfield and the stratum (sand). Unfortunately in commercial practice crudes are identified by the oilfield only; such designations as, for instance, East Texas or Oklahoma City, accepted in this book, would be insufficient if many producing sands were exploited in these fields. As a matter of fact, however, it is chiefly one producing stratum that is exploited, at least for the time given. Thus 'East Texas crude oil' means the crude oil produced from the Woodbine sand in East Texas; 'Oklahoma City crude oil' means the crude produced from the Wilcox sand in Oklahoma City, &c. Identification of Californian and Russian crudes is more difficult because several oil-bearing strata are exploited. Such designations as, for example, 'Light or Heavy Santa Fe Springs crude oil' show that the crudes are produced from different sands of the field.

There is no clear-cut relationship between the chemical composition of oils and their geological age or origin. It is frequently accepted that those which are geologically old, i.e. Devonian and Carboniferous, are paraffin- and mixed-base crudes, while those geologically new, such as Cretaceous or particularly Tertiary, are naphthenic or asphaltic. This generalization is more or less valid (with notable exceptions, however) in so far as the crude oils of the United States are concerned, but it seems to be untrue for oilfields of other countries. The Tertiary producing strata of Caucasian, Roumanian, and Polish fields yield asphaltic, naphthenic, and paraffinic crudes. In California, crude oils in the same pool are usually heavier and more asphaltic from the upper sands than those from the lower sands, according to the above generalization, whereas in Baku the opposite phenomenon is usually observed.

Commercial Classifications.

The classification of crude oils should be based on their chemical composition; any other classification based, for instance, upon the specific gravity or fractional composition would be artificial and misleading. According to the classification commonly accepted in the United States, crude oils are divided into two main groups: paraffin-base and asphaltic-base, depending upon the content of paraffin (petroleum) wax or asphalt, which can be easily determined.

From the commercial standpoint, true paraffin-base crudes on refining yield paraffin wax and no asphalt, whereas true asphaltic-base crudes yield no paraffin wax but are rich in asphalt. The distinction between the paraffin- and asphaltic-base crudes is, however, more fundamental than might be expected on the basis of the content of paraffin wax or asphaltic components. As is well known, the presence of petroleum wax determines in general the 'paraffinic' properties of all fractions, and, vice versa, a high asphaltic content is responsible for the so-called 'naphthenic' properties of all fractions.

While the distinction between the paraffin- and asphaltic-base oils is sufficiently sharp, it should be kept in mind that most crudes do not belong distinctly to either of these two types. Accordingly, the third type, the 'mixed-base', includes all oils having intermediate properties. This is the weak point of the classification, since practically 90% of petroleum of various properties and chemical composition is included in the broad and indefinite class of 'mixed-base' crudes.

The asphaltic-base class is frequently designated as 'naphthenic-base', in view of a misconception which was widely accepted a few years ago. It had been assumed that the paraffinic-base crudes not only contain paraffin wax, i.e. solid paraffin hydrocarbons, but consist almost entirely of paraffin hydrocarbons. In contrast to this, the asphaltic-base crudes were assumed to consist predominantly of cyclic or 'naphthenic' hydrocarbons. Accordingly, the mixed-base crudes were assumed to comprise a mixture of paraffinic and naphthenic hydrocarbons.

Smith and Lane [47*a*, 1928] have given some quantitative foundation to the commercial classification. In addition to this, the indefinite mixed-base class was subdivided into two narrower groups or classes. The classification was based upon the specific gravity of the fractions boiling between 250° and 275° C. or 482–527° F. (key fraction 1) and the cloud-point of the fraction boiling between 275° and 300° (527–572° F.) at 40 mm. pressure (key fraction 2). On this basis the crude oils were classified into 4 groups: paraffinic, intermediate, hybrid, and naphthenic.

Later, Lane and Garton [25, 1937] developed another classification on the basis of the specific gravity of both key fractions 1 and 2. The specific gravity of key fraction 1 determines the base of lighter fractions of the crude; that of key fraction 2 does the same for heavier fractions. For many crudes the base of both key fractions may be the same, and for others may be different, involving new types and classes of oils. Thus crude oils may be paraffinic in low-boiling fractions and 'naphthenic' in high-boiling fractions, and vice versa.

Thus the new classification divides the crude oils into nine classes or bases: paraffinic-paraffinic (or paraffinic), paraffinic-intermediate, paraffinic-naphthenic, &c. The classes paraffinic-naphthenic and naphthenic-paraffinic have not been recognized in any existing crude.

A serious shortcoming of any classification based on the specific gravity (or any other physical property) of fractions is the fact that the high specific gravity may be due to the presence of naphthenic and/or aromatic hydrocarbons. Actually both naphthenes and aromatics are associated in 'naphthenic' or cyclic group of hydrocarbons; thus a great difference between these two types of hydrocarbons has not been reflected in the classification. Moreover, high asphaltic crude oils, rich in sulphur and oxygen compounds, producing fractions of high specific gravity, are also classified as 'naphthenic' crude oils. Thus the class of 'naphthenic' crude oils actually includes quite different crudes: aromatic, naphthenic (in the chemical sense of the word), and asphaltic, or various mixtures of these types.

Chemical Classification.

An attempt to develop the chemical classification of crude oils on the basis of the content of various classes of hydrocarbons has been made by Sachanen and Virobianz. The crudes were classified according to the proportion of aromatic, naphthenic, and paraffin hydrocarbons in the distillates. The drawback to this classification was the disregard of resinous and asphaltic compounds which were associated with aromatic hydrocarbons.

A new attempt is being made to classify crude oils on the basis of more complete data on chemical composition available at the present time, including the data of ring analysis. The oils are classified according to the content of paraffinic constituents, i.e. paraffin hydrocarbons and paraffinic side chains, naphthenic and aromatic constituents, and resinous-asphaltic compounds. It should be pointed out that the term 'naphthenic' in this classification has the well-established chemical meaning, i.e. the saturated cyclic structures (in practice, the 5- and 6-ring structures, since the presence of other cyclic structures in petroleum has not been proved) and differs substantially from the same term in the classifications discussed above, in which it means the cyclic structure in general, embracing the naphthenic, aromatic, and asphaltic structures. It is believed that many misconceptions and shortcomings can be avoided by the use of the classification based on the chemical composition of crude oils.

The figures of the average composition of crude oils given below have been calculated from the data on the composition of various fractions, from gasoline to heavy lubricating fractions and residuum. These data, available for many crudes, are obtained by ring analysis and by the determination of aromatics, naphthenes, paraffins, and resinous-asphaltic constituents.

Both methods are applied to determine the chemical class of a crude oil. The ring-analysis data are particularly important for determining the paraffinic character or 'paraffinicity' of crude oils, since this property depends as much upon the content of paraffin hydrocarbons as upon that of paraffinic side chains. In addition, the percentage of resinous-asphaltic constituents is not determined by the ring analysis. Thus the data obtained by both methods must be used.

Ring-analysis data are usually lacking for residues containing a large proportion of neutral resins and asphaltenes. The conversion of the content of the resinous-asphaltic components into ring-analysis data has been made on the assumption that the resinous-asphaltic constituents would contain 40% aromatic rings, 27% naphthenic rings, and 33% paraffinic side chains (oxygen and sulphur being neglected).

The content of paraffin hydrocarbons in residues was accepted as equal to that of solid petroleum wax on the assumption that liquid paraffin hydrocarbons of branched structure are absent in residual oils. The distribution of aromatics, naphthenic rings, and paraffinic side chains in asphalt-free residues was taken to be the same as in the heaviest lubricating fraction for which ring-analysis data are available.

The determination of aromatic hydrocarbons by sulphonation gives fairly reliable results for all fractions. The determination of naphthenic and paraffin hydrocarbons is reliable for gasoline and for heavier fractions, in which the content of paraffin hydrocarbons is assumed to be equal to that of petroleum wax. The determination of naphthenes and paraffins in kerosine and light gas-oil distillates on the basis of aniline points or other physical properties is impossible. A direct determination of paraffins in these fractions is accompanied by many experimental difficulties because of the comparatively low melting-points of the paraffins in these distillates. Thus the content of paraffins and naphthenes in the kerosine and light gas-oil fractions was interpolated from the data for gasoline and heavier fractions.

It should be pointed out, however, that these more or less arbitrary assumptions do not appreciably affect the figures given below. In any case, the possible errors, owing to the assumptions involved, would not affect the general chemical character of a given crude oil nor change its place in the classification.

Paraffinic Crude Oils.

The basic chemical classes of crude oils are: paraffinic, naphthenic, aromatic, and asphaltic. Purely paraffinic crude oils of the conventional type, containing mostly paraffin hydrocarbons, are unknown. Natural gas, however, may be considered as a pure paraffinic gaseous crude of the same origin as conventional crude oils. Ozokerite is an almost pure paraffinic bitumen of the same origin. As far as physical properties are concerned, the condensates (from the condensate fields) are closer to conventional crude oils than is natural gas or ozokerite. The proportion of paraffins in the condensates is as high as 75%. The origin of the condensates, however, is different from that of crude oils and is due to the secondary condensation of gaseous constituents accumulated in reservoirs under pressure. For this reason, classification of the condensates with conventional paraffinic crude oils would be ambiguous.

The conventional paraffinic crude oils contain, in addition to paraffin hydrocarbons, a large proportion of cyclic hydrocarbons, predominantly naphthenes, with long paraffinic side chains. This class of crude oils is well defined also in other classifications, because the low specific gravity or C.I. of fractions is characteristic only of paraffin hydrocarbons or of cyclic hydrocarbons with long paraffinic side chains. The chemical composition of paraffinic crude oils may be represented as follows:

Paraffin hydrocarbons (including petroleum wax) .	40% (by weight)
Naphthenes	48%
Aromatics (sulphonatable)	10%
Resins and asphaltenes	2%

The paraffinic characteristic of the paraffinic crude oils is concealed to a certain extent by a high percentage of naphthenes which, however, have long paraffinic side chains. The ring analysis gives the following figures for the paraffinic crude oils:

Paraffinic side chains . .	78%
Naphthenic rings . .	16%
Aromatic rings . . .	6%

Thus the paraffinic character of the paraffinic crude oils is shown better by the ring-analysis data.

The paraffinic crude oils are represented in the United States by Pennsylvania, W. Virginia, Rodessa, and some other crude oils. It is of interest that the oilfields of other countries do not produce true paraffinic crudes in any substantial quantities.

Naphthenic Crude Oils.

Another chemically simple class of crude oils is the naphthenic group. Such crude oils are rare, and are represented in the United States only by some California crudes. The only representative of the naphthenic crude oils which has been thoroughly studied is the Emba-Dossor crude oil, the composition of which may be given as follows:

Paraffin hydrocarbons	12%
Naphthenes	75%
Aromatics.	10%
Resins and asphaltenes	3%

The ring analysis gives the following data:

Paraffinic side chains	63%
Naphthenic rings	30%
Aromatic rings	7%

In contrast to the paraffinic crude oils, the data of chemical analysis reflect the naphthenic character of the naphthenic oils better than the data of the ring analysis.

Many Baku crude oils are similar to the Emba crudes, but contain a higher percentage of other constituents at the expense of naphthenes. The composition of two such crude oils is given below:

	Balachany	*Bibi-Eibat*
Paraffin hydrocarbons	9	11
Naphthenes	66	60
Aromatics.	19	19
Resins and asphaltenes	6	10

While the Balachany crude oil is close to the Emba crude, the Bibi-Eibat crude is intermediate between the naphthenic and naphthenic-aromatic crude oils. It may not be a coincidence that the naphthenic crude oils are concentrated in the basin of the Caspian Sea.

Aromatic and Asphaltic Crude Oils.

The third simple class of crude oils would include the aromatic crudes which contain, say, 50% or more aromatic hydrocarbons. The crude oils of this class are not known. As will be seen later, even Borneo or Perm (Ural) crude oils only approach this class, being less aromatic and belonging to the mixed classes.

The last simple class of crude oils includes those which consist predominantly of resinous and asphaltic constituents, i.e. of oxygen-sulphur compounds. Crudes of this type are unknown, since the low- and medium-boiling distillates, present in crude oils, consist of hydrocarbons which decrease the percentage of resinous and asphaltic constituents. The natural asphalts or, better, the organic part of the natural asphalts, are bitumina which belong to the class in question. The chemical composition of a natural asphalt (Bermudez, penetration 25) may be represented as follows:

Paraffin hydrocarbons	5%
Naphthenes	15%
Aromatics.	20%
Resins and asphaltenes	60%

The liquid hydrocarbons of natural asphalts consist mostly of aromatics and naphthenes, which are polycyclic and have short paraffinic side chains.

As has been stated above, crude oils which are predominantly paraffinic, naphthenic, aromatic, or asphaltic are rather exceptional. Usually they contain at least two classes of these constituents which predominate over the others.

Paraffinic-Naphthenic Crude Oils.

The paraffinic-naphthenic class is widely distributed; many Mid-Continent crudes belong to this group, as, for instance, Oklahoma City or East Texas, the approximate composition of which is as follows:

	% by weight	
	Oklahoma City	*East Texas*
Paraffin hydrocarbons	36	33
Naphthenes	45	41
Aromatics	14	17
Resins and asphaltenes	5	9

The ring analysis gives the following figures:

	% by weight	
	Oklahoma City	*East Texas*
Paraffin side chains	65	60
Naphthenic rings	25	26
Aromatic rings	10	14

Of the two above Mid-Continent crudes, the Oklahoma City is more paraffinic than the East Texas. As in other mixed classes, there is a whole spectrum of paraffinic-naphthenic crudes, from those which are close to paraffinic crudes to those which are close to naphthenic crudes.

Naphthenic-Aromatic Crude Oils.

An increase in the content of aromatics at the expense of naphthenes would produce paraffinic-naphthenic-aromatic crude oils in which the percentage of each of the three classes of hydrocarbons is almost equal. The percentage of resinous and asphaltic compounds in these crudes is near 10%. Crudes of this type are comparatively rare, as, for instance, Maikop oils. In contrast to these, naphthenic-aromatic crudes are common, particularly those in which naphthenes predominate over aromatics. Many Gulf Coast and California crudes belong to this class. The composition of a light California crude oil (Santa Fe Springs) may be represented as follows:

Paraffin hydrocarbons	20%
Naphthenes	45%
Aromatics	23%
Resins and asphaltenes	12%

The ring analysis of the same crude oil gives the following data:

Paraffinic side chains	48%
Naphthenic rings	30%
Aromatic rings	22%

The naphthenic-aromatic crudes with an almost equal content of naphthenes and aromatics may be represented by Borneo crude oil. Its composition (sp. gr. about 0·85) is as follows:

Paraffin hydrocarbons	15%
Naphthenes	35%
Aromatics.	35%
Resins and asphaltenes	15%

Mixed Asphaltic Crude Oils.

Naphthenic-aromatic-asphaltic crude oils are also widely distributed. Many heavier Coastal and California, as well as Mexican and Venezuelan, crudes belong to this class. The composition of a heavy naphthenic-aromatic-asphaltic crude oil (sp. gr. 0·930, Inglewood) is:

Paraffins	8%
Naphthenes	42%
Aromatics.	27%
Resins and asphaltenes	23%

The very small proportion of paraffins is partially due to a low content of gasoline and other low-boiling fractions, which are comparatively rich in paraffins. If the crude oil of this class is of low specific gravity and contains a large proportion of gasoline, the percentage of paraffins will be somewhat larger, at the expense of other constituents. The percentage of paraffinic side chains in these classes of oils is small, and does not exceed 40%, indicating short paraffinic side chains and very low (negative) values of the viscosity index of high-boiling fractions.

Aromatic-asphaltic crude oils containing predominantly aromatic and asphaltic constituents occur less frequently than the representatives of the naphthenic-aromatic-asphaltic class. The Perm (Ural) crude belongs to the former class, as its composition clearly shows:

Paraffin hydrocarbons .	13%
Naphthenes . . .	15%
Aromatics. . . .	40%
Resins and asphaltenes .	32%

Apparently some heavy Mexican crude oils (e.g. Panuco) have a similar composition.

There are no crude oils which would belong to such mixed classes as paraffinic-aromatic or paraffinic-asphaltic. Table XXI summarizes the most important and frequent classes of crude oils. All existing crude oils may be classified in seven chemical classes or types.

TABLE XXI

Classification of Crude Oils

Class	*Composition*	*Crude oils*
Paraffinic	Percentage of paraffinic side chains 75% or more	Pennsylvania, Rodessa
Naphthenic	Percentage of naphthenic hydrocarbons 70% or more	Emba-Dossor
Aromatic	Percentage of aromatic hydrocarbons 50% or more	None
Asphaltic	Percentage of resins and asphaltenes 60% or more	(Bitumina of natural asphalts)
Paraffinic-naphthenic	Percentage of paraffinic side chains from 60 to 70%; percentage of naphthenic rings at least 20%	Many Mid-Continent crude oils
Paraffinic-naphthenic-aromatic	Percentage of paraffins, naphthenes, and aromatics approximately equal	Maikop
Naphthenic-aromatic	Percentage of naphthenes or aromatics 35% or more	Light Coastal and California crude oils
Naphthenic-aromatic-asphaltic	Percentage of naphthenes, aromatics, or asphaltic compounds 25% or more	Heavy Coastal and California crude oils
Aromatic-asphaltic	Percentage of aromatics or asphaltic compounds 35% or more	Ural, probably some heavy Mexican crude oils

REFERENCES

1. Alden, R. C., Frey, F. E., Hepp, H. T., and McReinolds, L. A. *Oil and Gas J.* 9 Feb. (1946).
2. Backer, H. I., and Strating, J. *Rec. Trav. Chim. Pay-Bas*, **59**, 933 (1940).
3. Bates, J. R., Kurtz, S. S., Rose, F. W., and Mills, I. W. *Ind. Eng. Chem.* **34**, 142 (1942).
3*a*. Boultbee, A. H. *Nat. Petr. News*, 2 Feb. (1944).
3*b*. Brown, R. A., Taylor, R. C., Melpolder, F. W., and Young, W. S. *An. Chem.* **20**, 5 (1948).
4. Buchler, C. C., and Graves, C. D. *Ind. Eng. Chem.* **19**, 718 (1927).
5. Callahan, J. R. *Chem. Eng.* Aug. (1946).
6. Carpenter, J. A. *J. Inst. Petr. Techn.* **12**, 288 (1926).
7. Clark, G. L., and Smith, M. A. *Ind. Eng. Chem.* **23**, 697 (1931).
8. Cosby, J. N., and Sutherland, L. M. *A.P.I. Proc.* Nov. (1941).
9. Egloff, G. *Physical Properties of Petroleum*, vol. 1 (1940).
10. Ferris, S. W., Cowles, M. C., and Henderson, L. M. *Ind. Eng. Chem.* **21**, 1090 (1929); **23**, 681 (1931).
11. Fischer, H. C. M., and Welty, A. B. *Chem. Met. Eng.*, Aug. (1944).
11*a*. Forziatti, A. B., and Rossini, F. D. *J. Res. Bureau of Standards*, **39**, 425 (1947).
12. Forziatti, A. B., Willingham, C. B., Mair, B. J., and Rossini, F. D. *Refiner*, Nov. (1943).
13. Francis, F. H., Watkins, C. W., and Wallington, W. R. *J. Chem. Soc.* 1529, 2804 (1922).
14. Frey, F. E., Matuczak, M. P., and Snow, R. D. U.S. Patent 2,186,524 (1940).
14*a*. Glasgow, A. R., Willingham, C. B., and Rossini, F. D. *J. Res. Bureau of Standards*, **38**, 621 (1947).
14*b*. ——— *St. Louis Meet., Amer. Chem. Soc.*, Sept. (1948).
15. Gooding, R. M., Adams, N. G., and Rall, H. T. *Ind. Eng. Chem. Anal. Ed.* **18**, 1 (1946).
16. Grosse, A. V., and Mavity, J. M. *Boston Meet. Amer. Chem. Soc.*, Sept. (1939).
17 Gurwitch, L. *Scientific Principles of Petroleum Technology* (London, 1934).
18. Hendrickson, L., Hutcheon, A. T., and Spinks, J. W. T. *J. Can. Res.* **20**, 31 (1942).
19. Holde, D., and Schunemann, K. H. *Z. angew. Chem.* **11**, 368 (1928).
20. Hufferd, R. W., and Kranz, H. A. *Boston Meet. Amer. Chem. Soc.*, Sept. (1939).
21. Komarewsky, V. I., and Riesz, C. H. *Oil and Gas J.* 24 June (1943).
22. Kolvoort, E. C. H., Moser, F. R., and Verver, C. G. *J. Inst. Petr.* **23**, 734 (1937).
23. Kraft, F. *Ber.* **21**, 2256 (1888); **40**, 4779 (1907).
24. Kurtz, S. S., and Lipkin, M. R. *Ind. Eng. Chem.* **33**, 779 (1941); *Detroit Meet. Amer. Chem. Soc.* (1940).
25. Lane, E. C., and Garton, E. L. R.I. 3279, Bureau of Mines, 1937, Washington, D.C.
26. Legatski, T. W., and Legatski, M. R. *Oil and Gas J.* 11 May (1946).
27. Leslie, R. T., and Heuer, W. W. *J. Res. Bureau of Standards*, **21**, 515 (1938).
28. Mabery, C. F. *Amer. Chem. J.* **33**, 285 (1905).
29. Mair, B. J., and Streiff, A. J. *J. Res. Bureau of Standards*, **24**, 395 (1940); **27**, 343 (1941).
30. Mair, B. J., and Schicktanz, S. T. *Ind. Eng. Chem.* **28**, 1056 (1936).
31. Mair, B. J., and Willingham, C. B. *J. Res. Bureau of Standards*, **17**, 923 (1936).
32. Mair, B. J., Willingham, C. B., and Streiff, A. J. Ibid. **21**, 536, 565, 581 (1938).
33. May, W. G., Miners, K. A., and Spinks, J. W. T. *J. Can. Res.* **21**, 73 (1943).
34. McKittrick, D. C., Henriques, H. J., and Wolff, H. I. *J. Petr. Inst.* **23**, 616 (1937).
34*a*. Mikeska, L. A. *Ind. Eng. Chem.* **28**, 970 (1936).
35. Müller, J., and Pilat, S. *J.I.P.T.* **21**, 887 (1935).
36. Nametkin, S. T., and Nifontova, S. S. *Chem. Zentr.* **1**, 1592 (1934); **11**, 3968 (1936).
37. Oberfell, G. G., and Frey, F. E. *Oil and Gas J.* 23–30 Nov. (1939).
38. O'Kelly, A. A., and Sachanen, A. N. *Ind. Eng. Chem.* **38**, 462 (1946).
39. Pogacnick, M. Diss. Technische Hochschule (Berlin, 1932).
40. Reistle, C. E., and Blade, O. C. Bull. 348, Bureau of Mines, Washington, D.C., 1932.
41. Rossini, F. D. *A.P.I. Proc.*, Nov. (1937); Nov. (1938).
41*a*. —— *Refiner*, Jan. (1947).
42. Rossini, F. D., Mair, B. J., Forziatti, A. B., Glasgow, A. R., and Willingham, C. B. *Refiner*, Nov. (1942).
43. Sachanen, A. N. *The Chemical Constituents of Petroleum*, p. 135 (New York, 1945).
44. Sachanen, A. N., and Bestougeff, N. A. *Petr. Zeit.* **22**, 484 (1926).
45. Sachanen, A. N., and Tilicheyev, M. D. *Ber.* **62**, 658 (1929).
46. Sachanen, A. N., and Virobianz, R. A. *Petr. Zeit.* **25**, 867 (1929); *Erdoel and Teer*, **9**, 170, &c. (1933).
47. Sachanen, A. N., Wassilieff, N. A., and Sherdeva, L. G. *Nat. Petr. News*, 22–9 Apr. (1931); 6–13 May (1931).
47*a*. Smith, N. A. C., and Lane, E. C. Bull. 291, Bureau of Mines, 1928, Washington, D.C.
47*b*. Streiff, A. J., and Rossini, F. D. *J. Res. Bureau of Standards*, **39**, 303 (1947).
48. Suida, H., and Planckh, R. *Ber.* **66**, 1445 (1933).
49. Tannich, R. E., Thomas, B. W., and Padgett, A. R. *Detroit Meet. Amer. Chem. Soc.*, Sept. (1940).
50. Tongberg, C. O., Nickels, J. E., Lawrosky, S., and Fenske, M. R. *Ind. Eng. Chem.* **29**, 571 (1937).
51. Varteressian, K. A., Fenske, M. R., and Smith, H. S. *Baltimore Meet. Amer. Chem. Soc.*, April (1939).
52. Yannaquis, N. *Ann. Comb. Liq.* **8**, 295 (1934); **13**, 1083 (1938).

THE CHEMISTRY OF PARAFFIN HYDROCARBONS

By J. HABESHAW

Anglo-Iranian Oil Co. Ltd.

Introduction

Recent researches into the chemistry of the paraffins have had two main objects. The first has been the production of high-performance fuels, especially aviation fuels, and the second the transformation of the paraffins to products useful as chemicals or chemical intermediates.

The superiority of the branched-chain paraffins as fuels for internal-combustion engines has led to the development of processes for the conversion of normal to isoparaffins. In the course of these developments a considerable knowledge of the isomerization reactions of the paraffins has been obtained. The very high performance of individual hydrocarbons such as 2,3-dimethylbutane (diisopropyl) and 2,2-dimethylbutane (neohexane) has led to the preparation of these hydrocarbons on a fairly large scale. The isomerization reactions utilized in the preparation of such hydrocarbons are mostly carried out on Friedel-Crafts catalysts, and their study has greatly increased our knowledge of the behaviour of hydrocarbons with these catalysts, especially with aluminium chloride [94, 1941].

The conversion of paraffins to aliphatic chemicals may be achieved either by direct reaction with such reagents as the halogens or nitrogen tetroxide, or by prior conversion by dehydrogenation to olefines or diolefines. The cyclization of the paraffins to aromatics makes them a potential source also of the whole range of aromatic chemicals. The outstanding example of the conversion of paraffins to chemicals is the conversion of butane to the butadiene required in synthetic rubber production. The catalytic cyclization of paraffins to aromatics is not yet equally important commercially, the dehydrogenation of naphthenes and alkylation of aromatics with olefines providing more economical methods for the production of the aromatics (chiefly toluene and special fuel components such as isopropylbenzene) required during the war. The vapour-phase nitration process developed by Hass and his collaborators has made available a new range of aliphatic chemicals derived from the lower nitroparaffins [36, 1943].

The great technical importance of the paraffins in processes such as those mentioned has led to the accumulation of a large amount of quantitative data. Largely by the work of Rossini and his collaborators [79, 1941; 80, 1945] the physical and thermodynamic properties of almost all the lower paraffins are known with some accuracy. The free-energy change of reactions involving the lower paraffins can thus often be calculated with accuracy, and the conditions under which various transformations may be expected to occur predicted, as was done, for example, by Taylor and Turkevich in studying the cyclization of paraffins to aromatics [92, 1939].

A great many measurements of reaction rates have been made, both from the theoretical point of view and to provide data for the technical development of such reactions as paraffin chlorination and the vapour-phase nitration. However, in many reactions, particularly those involving paraffins containing more than four carbon atoms, the identification of the products is often difficult owing to the number of possible isomers of very similar properties which may be produced. For this reason the point at which attack of the molecule by some reagents occurs is still not certain, notably in oxidations under certain conditions. In paraffin chemistry, therefore, kinetic measurements must be supplemented by identification and estimation of the relative proportions of the various products if a proper understanding of a reaction is to be obtained. The investigations into chlorination and vapour-phase nitration have added considerably to systematic knowledge of the constitution of the products of paraffin reactions. As a result of this and other work, some generalizations now appear well established. The reactivity of individual carbon atoms in a paraffin chain towards electrophilic reagents, including free radicals, increases in the order primary, secondary, and tertiary. The C—H bond strengths diminish in that order, as indicated by the heats of bromination determined by Conn, Kistiakowsky, and Smith [17, 1938]. In some cases the reaction rates found correlate well with data from independent sources. For example, the value of 102 Kcal./mole for the CH_3—H bond strength [53, 1944] and of 98 Kcal./mole [2, 1944] for the C_2H_5—H bond strength, obtained by Van Artsdalen, Anderson, and Kistiakowsky from the rates of bromination, agree well with values obtained by other methods.

Generally the relative reactivity of primary, secondary, and tertiary carbon atoms in the paraffins tends towards equality as the temperature is raised, as shown, for example, by the increasing importance of attack at the end carbon atom of the chain as the temperature is raised in oxidations and by the relative proportions of the respective mono-substituted products obtained at various temperatures in vapour-phase nitration and chlorination.

The position is a good deal less clear in the catalytic reactions. Whilst a catalyst must lower the energy barrier to be surmounted before reaction can occur, i.e. must reduce the activation energy of the reaction, the precise manner in which this is brought about is not generally known. The theoretical aspect of this question is discussed at length in the book of Glasstone, Laidler, and Eyring [28, 1941].

Some attempts have been made to formulate mechanisms of operation of catalysts in hydrocarbon reactions, one of the simplest and most general being that of Turkevich and Smith [98, 1946]; others will be referred to in subsequent paragraphs. None of the theories offers a completely satisfactory description of the observed facts, and chemical theory in hydrocarbons is considerably outstripped by technological practice. However, the extensive data now available on paraffin reactions makes them of great importance in general theoretical chemistry.

The following summarizes recent work on the more important paraffin reactions.

Halogenation of Paraffins

Rules governing the chlorination of paraffins were formulated some years ago by Hass and his collaborators [35, 1936]. Tertiary hydrogen atoms are most, secondary less, and primary least readily replaced by chlorine in the non-catalytic reaction. At 300° C. the ratios of primary, secondary, and tertiary substitution are 1·00:2·25:4·33, approaching 1:1:1 as the temperature is raised. Liquid-phase chlorination gives ratios obtainable only at much higher temperatures in the vapour phase, and the ratios are unchanged by the presence or absence of light, moisture, carbon surfaces, or solvents such as carbon tetrachloride. In forming monochlorides from long-chain paraffins it was found by Asinger [5, 1942] that the chlorine substituent distributes itself impartially over the methylene groups of the carbon chain, but substitution into the end methyl groups is relatively less. According to Hass [34, 1937] pressure increase as well as temperature rise decreases the ratio of secondary to primary hydrogens replaced. Too high a temperature or too long a contact time results in pyrolysis of the chlorides formed, primary chlorides pyrolysing least and tertiary most easily.

Production of polychlorides in the chlorination can be reduced by operating at a low conversion per pass. Rust and Vaughan [81, 1941] investigated the effect of a substituted chlorine on further substitution and found that the C—Cl group in a straight-chain aliphatic monochloride markedly retards further substitution on adjacent carbon atoms, the effect increasing with rise of temperature and extending to some extent to more remote carbon atoms.

Liquid-phase chlorination was found by Stauff [87, 1942] to be faster with a long-chain than a short-chain paraffin.

The kinetics of the high-temperature chlorination have been reviewed by Vaughan and Rust [102, 1940], and the chain character of the reaction under these conditions is generally accepted. The reaction is accelerated by agents, such as heat or light, capable of direct production of chlorine atoms from chlorine molecules, or by agents such as organic peroxides capable of forming free radicals which can produce the chlorine atoms from molecular chlorine [48, 1941].

It has been shown by Groll and Hearne that propylene under some conditions may be chlorinated to allyl chloride, the change from addition to substitution occurring with rise in reaction temperature [29, 30, 1939]. Vaughan and Rust found that the relative rates of substitution on to paraffin and olefine were such that the substitution of chlorine into ethane in an ethane-ethylene mixture may under some conditions be brought about without appreciable substitution into the ethylene [102, 1940].

In liquid-phase brominations Kharasch, Hered, and Mayo [51, 1941] found that, as with chlorinations, primary hydrogens are least and tertiary most readily replaced. With these brominations, however, some acceleration was obtained with oxygen, and no acceleration with peroxides.

The use of sulphuryl chloride as a chlorinating agent for paraffins has been reported by Kharasch and Brown [49, 1939; 50, 1942], the reaction being much accelerated by small amounts of organic peroxides, and the amount of substitution in various positions in the carbon chain following the same rules qualitatively as with the thermal or photochemical chlorination. With this reagent, the second chlorine atom tends to enter the molecule as far away from the first as possible.

The action of fluorine on the paraffins tends to be of explosive violence, and fluorinated hydrocarbons are generally prepared by reaction of chlorinated compounds with antimony trifluoride, fluorinated derivatives of propane being so obtained by Henne and Renoll [37, 1937]. Other fluorides have been used [16, 1938], and the direct formation of C_2F_6 from the elements has been reported by Simons and Block [86, 1937].

Halogenation of paraffins gives results agreeing well with the generalizations given in the introductory paragraph, and much systematic information on the reaction is available in the references cited.

Nitration of Paraffins

The liquid-phase nitration of paraffins has been known for many years; early investigators reported that it was accompanied by a large amount of oxidation as well as with the formation of a large proportion of polynitrocompounds. Mixed acid does not nitrate paraffins satisfactorily, nitric acid alone being much better. It is interesting that nitric acid alone with polymethylbenzenes is stated to give nitration in the methyl groups, while ring substitution occurs with mixed acid [36, 1943]. Titov [95, 1940] found that side-chain nitration of aromatics only occurs if the nitric acid contains oxides of nitrogen.

The vapour-phase nitration process for paraffins as developed by Hass and his collaborators takes place at much higher temperatures. Reaction begins around 270° C., but the optimum working temperature is 400° to 500° C. Vapour-phase nitration gives less paraffin oxidation and forms a greater proportion of mononitrocompounds than the liquid-phase reaction. The reaction rate and the proportion of primary mononitrocompounds formed increases with temperature, the variation of relative reactivity of primary, secondary, and tertiary carbon atoms with temperature thus following the same trend as in halogenations. As the yield of fission and oxidation products also increases with temperature, there is a quite critical optimum temperature for the reaction, and on a commercial scale the temperature for the nitration of propane is controlled to $\pm 1°$ F. The reaction has been investigated with methane [14, 1942], neohexane [45, 1946], and diisopropyl [18, 1944], and reviewed by Hass and Riley [36, 1943]. The results show that the products formed are generally those resulting from the replacement of all possible hydrogen atoms and alkyl groups by the nitro group, the relative amounts produced following the same qualitative rule as in halogenations for the relative reactivity of primary, secondary, and tertiary carbon atoms.

Although Hass and Riley cite a mechanism involving the formation of intermediate complexes [36, 1943] to explain the formation of optically active 3-nitro-3-methyloctane by the liquid-phase nitration of 1-3-methyloctane, McCleary and Degering from their study of the effect of the reaction variables in the vapour-phase nitration [62, 1938] regard a free radical mechanism as more likely under these conditions.

The vapour-phase nitration process is described in patents [32, 1937; 39, 1943], and the technological problems involved in the commercial process are discussed by Kirkpatrick [52, 1942].

No very successful catalysts for the nitration have so far been found. The effect of aluminium nitrate in liquid-phase nitrations appears to be merely to raise the boiling-point of the nitric acid [36, 1943], and catalysts which have been tried in the vapour-phase reaction increase the amount of oxidation at the expense of nitration.

Oxidation of Paraffins

Although there is a very large literature on the kinetics of paraffin oxidation, there is considerably less systematic information on the identity of the products formed under varying conditions. There is thus still some disagreement on the initial point of oxygen attack on the paraffin molecule. Whilst the data available does not appear inconsistent with the generalizations as to relative reactivity of primary, secondary, and tertiary carbon atoms given above, the factors governing the point of oxygen attack are complex. The problem has been recently discussed by Walsh [106, 1946].

In the liquid-phase oxidation of the higher paraffins at low temperatures, attack at the end carbon atom of the chain, as observed by Polly [73, 1946], is negligible. At higher temperatures, for example with the cool flame oxidation of propane as described by Newitt [67, 1937], appreciable end attack occurs, attack at the centre carbon atom of propane increasing with rise in pressure.

The mechanism most usually accepted at present assumes the formation of alkylhydroperoxides as primary products, although some authorities still prefer other mechanisms [107, 1946]. Assuming the order of reactivity of primary, secondary, and tertiary carbon atoms to be as found for halogenations and bearing in mind the slower rate of decomposition of tertiary alkylhydroperoxides, correlation of antiknock properties and oxidation characteristics of the paraffins is possible [106, 1946]. The hydroperoxide mechanism does not appear inconsistent with the formation of oxygen bridges as suggested by Polly [73, 1946] and earlier by Ubbelohde [101, 1935].

Low-temperature Liquid-phase Oxidation

The liquid-phase air oxidation of long-chain paraffins was used in Germany during the war to produce soap acids on a large scale. The process used has been described by Lanning and Clark [57, 1946]. A study of the reaction has been recently described by Polly [73, 1946]. Manganese salts are generally used as catalysts, although salts of cobalt and other metals are effective. The temperature used is 100–150° C., the oxidation yielding the whole homologous series of acids. Besides fatty acids, hydroxy-acids and esters are also formed, the proportions increasing with the percentage of the paraffin oxidized. The mean molecular weight of the product also decreases with the proportion of paraffin oxidized, so that in making soap acids the Germans oxidized only 30 to 50% of the charge, recycling unoxidized matter to the oxidation after removal of the acids. Although, according to Polly, a whole series of acids is formed, the greater part of the product corresponds to fission of the carbon chain at or near the centre. Attack at the end of the chain does not occur to any extent under these conditions.

Hexadecane has been oxidized under pressure at higher temperatures, alcohols, acids and other oxygen compounds being obtained on hydrogenation of the products [33, 1945]. The oxidation of lubricating oils is reviewed by Zuidema [109, 1946], and is not dealt with in this section.

'Cool Flame' Oxidations

The cool flame oxidation of paraffins occurs at temperatures between 300° and 400° C., the higher members being more readily attacked than methane or ethane. The reaction shows a pronounced induction period which decreases with rise in temperature; also, over a portion of the temperature range there is a negative temperature coefficient [96, 1937]. The use of pressures up to 100 atm. enables alcohols to be made in quite large yields by this reaction, according to the data of Newitt [67, 1937]. Wiezewich and Frolich [108, 1934] found that metallic catalysts can be used with advantage and gave a description of the pressure oxidations of the lower paraffins. Both Newitt and Frolich found that high pressures favoured the production of alcohols, while at lower pressures formaldehyde was a more important product.

The reaction has been applied to the oxidation of butane with air and steam to produce formaldehyde and higher oxygenated compounds [105, 1944], and to the oxidation of natural gas to formaldehyde and methanol [104, 1936; 13, 1945].

High-temperature Oxidations

The availability of cheap oxygen has made practicable the application of the reaction

$$CH_4+\tfrac{1}{2}O_2 = CO+2H_2$$

to the production of carbon monoxide from methane and other hydrocarbons. This reaction is the basis of the production of synthesis gas for the proposed 'Hydrocol' process for the production of synthetic hydrocarbons by a fluid catalyst version of the Fischer–Tropsch process. This has been recently described in general terms by Alden [1, 1946], but details of the reaction are not given.

The non-catalytic combustion of methane with oxygen under conditions of very short contact time was applied by the Germans to the production of a gas containing acetylene as well as carbon monoxide and hydrogen. The acetylene was converted into acetone [41, 1946; 60, 1946].

Catalytic Oxidations

Favourable results have been claimed for a great variety of catalysts in some of the oxidations described above, many references being given in the reviews of Egloff [20, 1937] and Marek [59, 1940]. The observation of Prettre [75, 1945] and his collaborators that in the high-temperature oxidation of methane with oxygen on a nickel catalyst the first reaction involves the complete consumption of all the available oxygen to form carbon dioxide and water, which then reacts further with excess methane to form carbon monoxide and hydrogen, illustrates the rapidity of reactions between paraffins and oxygen on catalysts of this type at high temperatures.

Reactions of Paraffins with Sulphur

As would be expected, the reactions of paraffins with sulphur have some resemblances to the oxidations, but are much less vigorous. Thacker and Miller [93, 1944] observed that with methane, carbon bisulphide is formed without extensive side reactions at temperatures below 700° C. using catalysts such as silica gel. It was found by Rasmussen, Hansford, and Sachanen [76, 1946] that paraffins and sulphur react to form thiophenes, olefines, and diolefines at 600–700° C. without a catalyst, the reaction being much milder and more easily controlled than with oxygen. Friedmann [26, 1941] describes the formation of thiophanes, thiophenes, and complex ring compounds and polysulphides by reaction of paraffins with sulphur.

Dehydrogenation of the Paraffins

Paraffins may be dehydrogenated on metallic catalysts such as cobalt and nickel and on metallic oxides. The behaviour of metallic catalysts is described by Komarewsky and Riesz [55, 1939]. They are active at lower temperatures than the oxide catalysts and isomerization of the paraffin also occurs. Much academic work has been done with the simpler metallic catalysts to establish a theoretical basis for the catalytic reactions of the lower hydrocarbons such as ethane and ethylene, e.g. that of Twigg and Rideal [99, 1941; 100, 1938], but the oxide catalysts have been most studied from the technical point of view. Oxides of chromium or molybdenum, usually supported on alumina, are generally used as dehydrogenation catalysts, although other catalysts have been found to have activity, as described, for instance, by Moldavskii and his collaborators [64, 1937]. The paraffins below hexane form olefines or diolefines according to the conditions of temperature and pressure; with higher paraffins, cyclization to aromatics also occurs. The most important application at present is the conversion of butanes to butene and butadiene, a subject reviewed by Egloff and Hulla [21, 1944]. Thermodynamic considerations show, as pointed out by Taylor and Turkevich [92, 1939], that the conversion of paraffins to aromatics is likely to occur in the temperature range 300–600° C. The reaction has been found to occur with heptanes and octanes within this range. The efficiency of promoted chromium oxide catalysts for this reaction has been investigated by Archibald and Greensfelder [3, 1945]; the efficiency of the catalysts declines with use, probably owing to the deposition of high molecular weight compounds on the surface. These may be burned off with air or oxygen without harm to the catalyst if the temperature during this treatment is not allowed to rise too high [97, 1944]. It was found by Mattox in the conversion of heptane to toluene that water vapour and ethylene retard the reaction, the effect on the relative rates of formation of olefines and aromatics being the same as with the usual decline of catalyst activity with use [91, 1941; 89, 1945]. It is generally accepted as suggested by Pitkethly and Steiner [71, 1939] that the half-hydrogenated transition stage or the olefines themselves, which are always found in the products, are intermediates in the formation of aromatics. In no case has any appreciable formation of naphthenes been observed in these cyclizations of paraffins, although the rate of dehydrogenation of these to aromatics under the usual conditions, while faster than the rate of formation of aromatics from paraffins, is relatively sufficiently slow to allow of their ready detection if actually formed as intermediates, as indicated by Hoog and co-workers [42, 1939] and Komarewsky and Shand [56, 1944]. Hoog, Verheus, and Zuiderweg [42, 1939] also observed that the rate of cyclization of the olefines was greater than that of the paraffins of corresponding structure. The failure of Hoog and his collaborators [42, 1939] to cyclize paraffins such as 2,2,4-trimethylpentane, whose structure does not permit of direct ring formation, was due to their use of too low a reaction temperature, since these paraffins have since been cyclized by Herington and Rideal [38, 1945], using a temperature of 550° C. It is suggested by Steiner [88, 1939] and Herington and Rideal that the rate of cyclization of a paraffin depends on the number of possible modes of cyclization. To form the products observed from many paraffins, isomerization must occur at some stage of the process, and it is likely that this happens during the actual ring formation, as stated by Komarewsky and Shand [56, 1944] and Herington and Rideal, the latter authors putting forward a detailed mechanism of cyclization [38, 1945]. Hoog, Verheus, and Zuiderweg found that the olefines formed in these dehydrogenation reactions tended to have the double bond near the centre of the chain; possibly the olefines finally appearing in the product are produced by isomerization of other olefines formed as primary products [42, 1939].

The dehydrogenation of higher paraffins has been less studied from the point of view of olefine production. Balandin [8, 1943] studied the dehydrogenation of a solid paraffin on chromia and found that dehydrogenation to olefine, fission of the molecule to paraffin plus olefine, formation of aromatics, and complete cracking to methane all took place. The formation of olefines increased with rise in temperature, but so did the extent of cracking.

Isomerization of Paraffins

The demand for isoparaffins for use in aviation fuels has led to the development of chemical processes for the conversion of the naturally more abundant straight-chain paraffins to branched chain compounds. Thermodynamically the more highly branched isomers are most stable at low temperatures, the stability of the normal with respect to other isomers rising with increase of temperature, as shown by Rossini and his collaborators [79, 1941; 80, 1945; 70, 1946]. Experimental figures of Schuit and Pines and their co-workers [84, 1940; 69, 1945] are in agreement with the thermodynamically calculated figures. As the isoparaffins are most stable at low temperatures, it is fortunate that the most successful catalysts for paraffin isomerizations are effective generally below 150° C. Friedel–Crafts catalysts such as boron trifluoride, zirconium fluoride, but especially aluminium halides, are good catalysts. The catalyst most commonly used in practice is aluminium chloride. Other catalysts such as the oxides of tungsten and molybdenum and metals like cobalt and nickel have some activity at higher temperatures, but are much less efficient than aluminium chloride [47, 1938].

Earlier work on isomerization reactions is summarized in the monograph by Egloff, Hulla, and Komarewsky [23, 1942]. With aluminium halides, a promoter is necessary, hydrogen halides being most usually employed, and in the complete absence of promoters no isomerization occurs. Schmerling, Pines, and others have shown that alkyl halides, olefines [12, 1946], oxygen [70, 1946], and water [103, 1946] will all function as promoters. Only with butane is it possible in practice to carry out the isomerization on crystalline aluminium chloride [66, 1937] or on aluminium chloride deposited on a porous support [15, 1946; 24, 1943] with the practical exclusion of side reactions. With pentane, as observed by Glasebrook, Phillips, and Lovell [27, 1936], appreciable decomposition occurs, the main decomposition product being isobutane, and the aluminium chloride is converted into a liquid tarry complex. For the isomerization of pentanes and hexanes these liquid complexes, generally with added aluminium chloride, are used as catalysts. With pentane, the extent of the decomposition reactions can be reduced by the addition of benzene as described by Armistead [4, 1946] or cyclic compounds [85, 1944]. With hexanes, the decomposition reactions are largely reduced by the use of high hydrogen pressures as described by Swearingen, Gekler, and Nysewander [90, 1946] and Koch and Richter [54, 1944]. The extent of the decomposition increases with rise in temperature, and is greater with aluminium bromide than with the chloride, so that decomposition of butane also occurs if the conditions be sufficiently severe. In the decomposition reaction, higher as well as lower paraffins are formed. It was, for instance, shown by Moldavskii and others [65, 1944] that pentane yields hexanes as well as butane, the hexanes containing appreciable amounts of 2,2-dimethylbutane. The reaction is not, however, a stoichiometric disproportionation, as is shown by the results of Bishop and Grumitt and their collaborators [11, 1945] and by the data given in the review of Egloff, Wilson, Hulla, and Van Arsdale [22, 1937].

The formation of neopentane in pentane isomerization reactions has not been observed, and whilst the conversion of *n*-hexane to 2-methylpentane and 3-methylpentane is easily brought about, conversion to 2,2-dimethylbutane has proved much more difficult, and requires conditions of such severity that its formation without appreciable decomposition of hexanes is very difficult. Bishop [11, 1946] indeed has stated that the amount of this hydrocarbon produced from other hexanes can be correlated with the amount of cracking taking place, and that 2,2-dimethylbutane does not itself isomerize to any appreciable extent.

There is little systematic data on the isomerization of paraffins higher than hexane. With these compounds, and indeed with hexane, the position is often complicated by the presence of cyclic compounds in the feedstocks used. It is clear, however, that isomerization does occur, some of the branched chain paraffins isomerizing to one another with great ease. Birch and Besley [10, 1943], for example, found that the interconversion of 2,3- and 2,4-dimethylpentane occurred on simply stirring with sulphuric acid. With heptanes and octanes also it is very difficult to separate the useful from the less useful isomers, even though isomerization does occur. Thus the very valuable triptane is not easily separated from the less valuable 2,2- and 2,4-dimethylpentanes.

From the very numerous experimental studies of isomerization reactions it appears that the acid $HAlCl_4$ is the true catalytic agent [58, 1943; 74, 1945], and Turkevich and Smith point out that this brings the reactions into line with their general mechanism for a number of hydrocarbon reactions [98, 1946]. The general theory involving carbonium ions put forward by Schmerling [82, 1944] and the similar views of Bartlett, Condon, and Schneider [9, 1944] on alkylation reactions provide an alternative mechanism to that of Turkevich and Smith.

Paraffin Alkylations

The sulphuric acid catalysed alkylation of paraffins with olefines is dealt with elsewhere; here a few special condensations are briefly summarized.

From the practical point of view the most important of these is the condensation of ethylene with isobutane. This, which does not go well with sulphuric acid as catalyst, has been successfully carried out on aluminium chloride. The main product was shown by Grosse and Ipatieff to be 2,3-dimethylbutane [31, 1943]. The condensation has been carried to the pilot plant scale, as described by Holloway and Bonnell [40, 1946], and is a more satisfactory method of making diisopropyl than isomerization since the hydrocarbon can be obtained in high concentration by the condensation, which is not possible by the isomerization. Coupling of the unsaturated compound at the tertiary carbon of the paraffin should give 2,2-dimethylbutane, which is in fact the product obtained in the non-catalytic condensation carried out by Frey and Hepp [25, 1936] and in the vapour-phase condensation with the homogeneous catalysts of O'Kelly and Sachanen [68, 1946] carried out at high temperatures and pressures. The proportion of 2,3-dimethylbutane obtained in the aluminium chloride catalysed condensation could not be obtained by isomerization of neohexane formed as primary product, since neohexane under these conditions is more stable than diisopropyl and moreover neohexane does not readily isomerize on aluminium halides [11, 1945]. Schmerling [82, 1944] suggests that the reaction proceeds through the alkyl halides, claiming that his results on the reaction of tertiary butyl chloride with ethylene [83, 1945] are consistent with this explanation. Similar ideas involving exchange of halogens and hydrogen between alkyl halides and paraffins are put forward more generally by Bartlett, Condon, and Schneider [9, 1944].

O'Kelly and Sachanen found that small amounts of compounds of oxygen, nitrogen, and halogens will catalyse the condensation of paraffins and olefines at high temperatures and pressures. The products obtained are those expected by reaction of the unsaturated compound at the primary and secondary carbon atoms of the paraffin. Although one of the objects of the work was the production of triptane, this hydrocarbon was obtained only in very low yield by this reaction.

A number of less important condensations have been reported. According to Hopff and his co-workers, amides of carboxylic acids are formed by the condensation of carbamyl chloride with paraffins [43, 1939], and with carbon monoxide ketones are formed. Paraffins and acid chlorides also condense to form ketones, but the reaction is slow [44, 1936].

Sulphonation and Chlorsulphonation of Paraffins

Most paraffins will react, although often very slowly, with sulphuric acid. With branched chain compounds such as isooctane the reverse reaction to alkylation can occur.

The Reed photochemical chlorsulphonation of paraffins with sulphur dioxide and chlorine [77, 1936] was studied in Germany and used on a large scale during the war. The products RSO_2Cl were called Mersols and were widely used for the preparation of detergents and cutting oils in Germany [7, 1946; 78, 1946]. The reaction is a general one, isobutane yielding the sulphonyl chloride with only a small proportion of direct substitution of chlorine into the paraffin, as found by Asinger and Eberneder [6, 1942].

An alternative reaction was studied in Germany, using SO_2 and oxygen for the preparation of sulphonic acids from the paraffins. This required continuous irradiation with ultra-violet light, but it was discovered that this continuous irradiation could be dispensed with by carrying out the reaction in the presence of small quantities of acid anhydrides, acid chlorides or ketones, acetic anhydride being preferred. This, the Hostapon process, was developed to the pilot plant scale in Germany [7, 1946]. Per-anhydrides, some of which were isolated, are formed as intermediate products in the reaction.

Miscellaneous Paraffin Reactions

An important general reaction has been recently reported by Ipatieff and Haensel [46, 1946]. They have found that on cobalt and nickel catalysts methyl groups attached to secondary carbon atoms are much more readily removed than methyl groups attached to tertiary carbons, methyl groups attached to quaternary carbons being least easily detached. Thus isopentane yields on demethylation in this way much more isobutane and 2,2,3-trimethylpentane much more triptane than would be the case if the demethylation were not selective.

The reaction reported by Mitchell and Carson [63, 1936] between nitrosyl chloride and *n*-hexane is of some interest. Methyl-*n*-propyl ketone and methyl-*n*-butyl ketone are formed in about equal proportions and the reaction is much accelerated by light.

REFERENCES

1. Alden, R. C. *Oil Gas J.* **45**, 79 (Nov. 1946).
2. Anderson, H. C., and Van Artsdalen, E. R. *J. Chem. Phys.* **12**, 469–78 (1944).
3. Archibald, A. C., and Greensfelder, B. S. *Ind. Eng. Chem.* **37**, 356–61 (1945).
4. Armistead, G. *Oil Gas J.* **45** (22), 82 (1946).
5. Asinger, F. *Ber.* **75b**, 668–75 (1942).
6. Asinger, F., and Eberneder, F. *Ber.* **75b**, 344–9 (1942).
7. Baird, W. B.I.O.S. Final Report No. 478, *Textile Auxiliary Products, Development of Mersol and Hostapon Process by I.G. Farbenindustrie, Hochst.* H.M. Stationery Office, London (1946).
8. Balandin, A. A., and Marushkin, M. M. *Compt. rend. Acad. Sci., U.R.S.S.* **40**, 226–8 (1943).
9. Bartlett, P. D., Condon, F. E., and Schneider, A. *J. Am. Chem. Soc.* **66**, 1531 (1944).
10. Birch, S. F., and Besley, D. M. Brit. Pat. 550,389 (6 Jan. 1943).
11. Bishop, J. W., Burk, R. E., and Lankelma, H. P. *J. Am. Chem. Soc.* **67**, 910–15, 915–18 (1945).
12. Block, H. S., Pines, H., and Schmerling, L. *J. Am. Chem. Soc.* **68**, 153 (1946).
13. Bludworth, J. E. U.S. Pat. 2,369,710 (20 Feb. 1945).
14. Boyd, T., and Hass, H. B. *Ind. Eng. Chem.* **34**, 300 (1942).
15. Cheyney, H. A., and Raymond, C. L. *Trans. Am. Inst. Chem. Engrs.* **42**, 573–609 (1946).
16. Clarke, F. H. U.S. Pat. 2,122,278 (28 June 1938).
17. Conn, J. B., Kistiakowsky, G. B., and Smith, E. A. *J. Am. Chem. Soc.* **60**, 2764–79 (1938).
18. Danzig, M. H., and Hass, H. B. *J. Am. Chem. Soc.* **66**, 2017–19 (1944).
19. Dunphy, R. A. Can. Pat. 370,106 (23 Nov. 1937).
20. Egloff, G. *J. Inst. Pet.* **23**, 645 (1937).
21. Egloff, G., and Hulla, G. *Chem. Reviews*, **35**, 279–333 (1944).
22. Egloff, G., Wilson, E., Hulla, G., and Van Arsdale, P. H. *Chem. Reviews*, **20**, 345–411 (1937).
23. Egloff, G., Hulla, G., and Komarewsky, V. I. *Isomerisation of Pure Hydrocarbons.* A.C.S. Monograph, No. 88 (1942).
24. Fawcett, E. W. M., and Jenkins, G. I. Brit. Pat. 556,895 (27 Oct. 1943).
25. Frey, F. E., and Hepp, H. T. *Ind. Eng. Chem.* **28**, 1439 (1936).
26. Friedmann, W. *Refiner*, **20** (10), 395–406 (1941).
27. Glasebrook, L., Phillips, N. E., and Lovell, W. G. *J. Am. Chem. Soc.* **58**, 1944–8 (1936).
28. Glasstone, S., Laidler, K. J., and Eyring, H. *The Theory of Rate Processes.* McGraw-Hill Book Co., Inc., chap. vi (1941).
29. Groll, H. P. A., and Hearne, G. *Ind. Eng. Chem.* **31**, 1530–7 (1939).
30. Groll, H. P. A., Hearne, G., Rust, F. F., and Vaughan, W. E. *Ind. Eng. Chem.* **31**, 1239–44 (1939).
31. Grosse, A. V., and Ipatieff, V. N. *J. Org. Chem.* **8**, 438–47 (1943).
32. Hass, H. B., and Hodge, E. B. U.S. Pat. 2,071,122 (16 Feb. 1937).
33. Hass, H. B., McBee, E. T., and Churchill, J. W. *Ind. Eng. Chem.* **37**, 445–8 (1945).
34. Hass, H. B., McBee, E. T., and Hatch, L. F. *Ind. Eng. Chem.* **29**, 1335–8 (1937).
35. Hass, H. B., McBee, E. T., and Weber, P. *Ind. Eng. Chem.* **28**, 333 (1936).
36. Hass, H. B., and Riley, E. F. *Chem. Reviews*, **32**, 373–430 (1943).
37. Henne, A. L., and Renoll, M. W. *J. Am. Chem. Soc.* **59**, 2434–6 (1937).
38. Herington, E. F. G., and Rideal, E. K. *Proc. Roy. Soc. (London)*, A **184**, 450 (1945).
39. Hodge, E. B. U.S. Pat. 2,327,964 (24 Aug. 1943).
40. Holloway, C., and Bonnell, W. S. *Ind. Eng. Chem.* **38**, 1231–8 (1946).
41. Holroyd, R. C.I.O.S. Report, File No. XXX-103, *I.G. Farbenindustrie, A.G. Works, Ludwigshafen and Oppau.* H.M. Stationery Office, London (1946).
42. Hoog, H., Verheus, J., and Zuiderweg, F. *Trans. Far. Soc.* **35**, 993–1006 (1939).
43. Hopff, H., Kellerman, H., and Freytag, A. U.S. Pat. 2,168,161 (1 Aug. 1939).
44. Hopff, H., Nenitzescu, C. D., Isacescu, D. A., and Cantuniari, I. D. *Ber.* **69**, 2244–51 (1936).
45. Howe, A. P., and Hass, H. B. *Ind. Eng. Chem.* **38**, 251–3 (1946).
46. Ipatieff, V. N., and Haensel, V. *J. Am. Chem. Soc.* **68**, 345–6 (1946).
47. Ipatieff, V. N., and Pines, H. Paper presented before the Petroleum Division of the A.C.S., Dallas Meeting, April 1938.
48. Kharasch, M. S., and Berkmann, M. G. *J. Org. Chem.* **6**, 810–17 (1941).
49. Kharasch, M. S., and Brown, H. C. *J. Am. Chem. Soc.* **61**, 2142 (1939).
50. ——— U.S. Pat. 2,302,228 (17 Nov. 1942).
51. Kharasch, M. S., Hered, W., and Mayo, F. R. *J. Org. Chem.* **6**, 818–29 (1941).
52. Kirkpatrick, S. D. *Chem. Met. Eng.* **49**, 129 (1942).
53. Kistiakowsky, G. B., and Van Artsdalen, E. R. *J. Chem. Phys.* **12**, 469–78 (1944).
54. Koch, H., and Richter, H. *Ber.* **75b**, 127–32 (1944).
55. Komarewsky, V. I., and Riesz, C. H. *J. Am. Chem. Soc.* **61**, 2524 (1939).
56. Komarewsky, V. I., and Shand, W. C. *J. Am. Chem. Soc.* **66**, 1118–19 (1944).
57. Lanning, M. J., and Clark, G. C. B.I.O.S. Final Report, No. 748, *Manufacture of Fatty Acids by Oxidation of Paraffins, Hydrogenation of the Fatty Acids at I.G. Ludwigshafen–Oppau.* H.M. Stationery Office, London (1946).
58. Leighton, P. D., and Heldman, J. D. *J. Am. Chem. Soc.* **65**, 2276–80 (1943).
59. Marek, L. F. *12th Report of the Committee on Catalysis, National Research Council*, p. 145 (1940).
60. Matthews, M. A., and Wood, W. L. B.I.O.S. Final Report, No. 877, *Oxidation of Hydrocarbons to Ethylene and of Methane to Acetylene, with Conversion of Acetylene to Acetone, I.G. Oppau.* H.M. Stationery Office, London (1946).
61. Mattox, W. J. *J. Am. Chem. Soc.* **66**, 2059 (1944).
62. McCleary, R. F., and Degering, E. F. *Ind. Eng. Chem.* **30**, 64 (1938).
63. Mitchell, S., and Carson, S. C. *J. Chem. Soc.* 1005 (1936).
64. Moldavskii, B. L., Kamusher, M. D., and Kobyl'skaya. *J. Gen. Chem. (U.S.S.R.)*, **7**, 1835–9 (1937).
65. Moldavskii, B. L., Nebylova, E., and Nozokina, T. *J. Gen. Chem. (U.S.S.R.)*, **14**, 343 (1944).
66. Montgomery, C. W., McAteer, J. H., and Franke, N. W. *J. Am. Chem. Soc.* **59**, 1768 (1937).
67. Newitt, D. M. *Chem. Reviews*, 299–317 (1937).
68. O'Kelly, A. A., and Sachanen, A. N. *Ind. Eng. Chem.* **38**, 463–7 (1946).
69. Pines, H., Kvetinskas, B., Kassel, L. S., and Ipatieff, V. N. *J. Am. Chem. Soc.* **67**, 631–7 (1945).
70. Pines, H., and Wackher, R. C. *J. Am. Chem. Soc.* **68**, 595 (1946).
71. Pitkethly, R. C., and Steiner, H. *Trans. Far. Soc.* **35**, 979–84 (1939).
72. Pitzer, K. S., and Kilpatrick, J. E. *Chem. Reviews*, **39**, 435–81 (1946).
73. Polly, O. L. Paper presented before the Petroleum Division of the A.C.S., Atlantic City Meeting, April 1946.
74. Powell, T. M., and Reid, F. B. *J. Am. Chem. Soc.* **67**, 1020–6 (1945).
75. Prettre, M., Eichner, C., and Perrin, M. *Trans. Far. Soc.* **42**, 335–9 (1945).
76. Rasmussen, H. C., Hansford, R. C., and Sachanen, A. N. *Ind. Eng. Chem.* **38**, 376–82 (1946).
77. Reed, C. F. U.S. Pat. 2,046,090 (30 June 1936).
78. Richardson, R. E., Kern, J. G., Murray, R. L., and Sudhoff, R. W. C.I.O.S. Report, Item No. 22, File No. XXVI-2, *Synthetic Emulsifying Agents, Wetting Agents, Detergents and Soap Substitutes.* H.M. Stationery Office, London (1946).
79. Rossini, F. D., Prosen, E. J., and Pitzer, K. S. *J. Res. Nat. Bur. S.* **27**, 529 (1941).
80. ——————— *J. Res. Nat. Bur. S.* **34**, 255–63 (1945).
81. Rust, F. F., and Vaughan, W. E. *J. Org. Chem.* **6**, 479–87 (1941).
82. Schmerling, L. *J. Am. Chem. Soc.* **66**, 1423 (1944).
83. —— *J. Am. Chem. Soc.* **67**, 1152–3 (1945).
84. Schuit, C. A., Hoog, H., and Verheus, J. *Rec. Trav. Chim.* **59**, 806–9 (1940).
85. Shell Development Co. Brit. Pat. 559,426 (18 Feb. 1944).
86. Simons, J. H., and Block, L. D. *J. Am. Chem. Soc.* **59**, 1407 (1937).
87. Stauff, J. *Z. Elektrochem.* **48**, 550–9 (1942).
88. Steiner, H. *Trans. Far. Soc.* **35**, 1008 (1939).
89. —— *J. Am. Chem. Soc.* **67**, 2052 (1945).
90. Swearingen, J. E., Gekler, R. D., and Nysewander, C. W. *Trans. Am. Inst. Chem. Engrs.* **42**, 573–95 (1946).

91. Taylor, H. S., and Fehrer, H. *J. Am. Chem. Soc.* **63,** 1387 (1941).
92. Taylor, H. S., and Turkevich, J. *Trans. Far. Soc.* **35,** 921–34 (1939).
93. Thacker, C. M., and Miller, E. *Ind. Eng. Chem.* **36,** 182–4 (1944).
94. Thomas, C. A. *Anhydrous Aluminium Chloride in Organic Chemistry,* A.C.S. Monograph, No. 87 (1941).
95. Titov, A. I. *J. Gen. Chem.* (*U.S.S.R.*), **10,** 1878–84 (1940).
96. Townend, D. T. A. *Chem. Reviews,* **21,** 260 (1937).
97. Turkevich, J. *J. Chem. Phys.* **12,** 345–7 (1944).
98. Turkevich, J., and Smith, R. K. *Nature,* **157,** 874 (1946).
99. Twigg, G. H. *Proc. Roy. Soc.* (*London*), A **178,** 106 (1941).
100. Twigg, G. H., and Rideal, E. K. *Proc. Roy. Soc.* (*London*), A **171,** 55 (1938).
101. Ubbelohde, A. R. *Proc. Roy. Soc.* (*London*), A **152,** 354 (1935).
102. Vaughan, W. E., and Rust, F. F. *J. Org. Chem.* **5,** 447–72 (1940).
103. Wackher, R. C., and Pines, H. *J. Am. Chem. Soc.* **68,** 1642 (1946).
104. Walker, J. C. U.S. Pat. 2,042,134 (26 May 1936).
105. Walker, J. F. *Formaldehyde,* A.C.S. Monograph, No. 98, p. 16 (1944).
106. Walsh, A. D. *Trans. Far. Soc.* **42,** 269–79 (1946).
107. Waters, W. A. *Trans. Far. Soc.* **42,** 184–9 (1946).
108. Wiezewich, P. J., and Frolich, P. K. *Ind. Eng. Chem.* **26,** 267–76 (1934).
109. Zuidema. *Chem. Reviews,* **38,** 197–227 (1946).

THE CHEMISTRY OF NAPHTHENE HYDROCARBONS

By W. J. OLDHAM

Anglo-Iranian Oil Co. Ltd.

Naphthenes

THE chemistry of the saturated cyclic hydrocarbons is, in the main, similar to that of the paraffin hydrocarbons, but the differences in stability of compounds containing different-sized rings prevent the formulation of any reliable generalizations concerning their chemical properties. The most stable naphthenes are those containing five- or six-membered rings since ring structures of this size are comparatively free from strain. Cyclopropane, on the other hand, is a highly strained compound and breaks down in some reactions to give *n*-propyl derivatives.

The dialkyl substituted naphthenes can exist in *cis* and *trans* forms, and these usually possess boiling-points which differ by a few degrees. The refractive indices and densities of the stereo-isomers are also different. The spatial configuration of many of these isomers cannot be regarded as definitely established. Zelinsky [44, 1902] carried out a small-scale asymmetric synthesis of 1,3-dimethylcyclohexane and obtained this hydrocarbon in an optically active form. This compound, which had the boiling-point of the lower-boiling isomer, was therefore assigned the *trans* configuration since the *cis* compound cannot exhibit optical activity. In his work on the synthesis of various 1,2-dialkylcyclopentanes, Chiurdoglu [13, 1932; 14, 1933; 15, 1934; 16, 1938] also states that the lower-boiling isomers have the *trans* configuration. Mousseron and Granger, however [36, 1938], also carried out an asymmetric synthesis of 1,3-dimethylcyclohexane and found that the higher-boiling isomer was optically active and this isomer was therefore assigned the *trans* configuration. Chiurdoglu [17, 1944] subsequently compared the relative rates of reaction of various 1,2-dialkylcyclopentanes towards reagents such as bromine and potassium permanganate and found that, as with the 1,3-dimethylcyclohexanes, the higher-boiling isomers reacted the more rapidly. Using the configuration of the 1,3-dimethylcyclohexanes as determined by Mousseron and Granger [loc. cit.], Chiurdoglu concluded, on these grounds of comparable chemical reactivity, that the higher-boiling 1,2-dialkylcyclopentanes had the *trans* configuration.

It appears to be generally assumed that the *cis* compound is the higher-boiling isomer, but Chiurdoglu [17, 1944] states that argument on the basis of physical properties gives misleading conclusions and that comparison of chemical reactivity gives more consistent results. In view of these conflicting reports on the structure of the dialkylnaphthenes it is obvious that the present position is unsatisfactory and that further work must be done definitely to establish the configuration of any one compound.

Halogenation of Naphthenes

The halogenation of naphthenes has been described by Thorpe and Farmer [40, 1938]. Kharasch and co-workers [28, 31, 1941] have since studied the effects of light and oxygen on the reaction between naphthenes and halogens. It was found that the chlorination of cyclohexane proceeded slowly at 0° C. in the absence of light and catalysts. In the presence of light, the reaction was very rapid, 100% of the chlorine being absorbed in less than a minute. The reaction in the dark is accelerated by a peroxide, such as ascaridole, but oxygen completely inhibits the absorption of chlorine. When both oxygen and ascaridole are present, the inhibitory effect of oxygen outweighs the accelerative effect of ascaridole.

The reaction between bromine and cyclohexane and methylcyclohexane is also very slow in the absence of both light and oxygen. This bromination is, however, greatly accelerated in the presence of either light or oxygen, and in the presence of both the effect is far greater than the sum of the individual effects. The combined effects of light and oxygen are in fact more nearly equal to the product of the individual effects rather than to their sum. The presence of peroxides such as lauroyl and benzoyl peroxide has very little accelerating effect.

The speed of reaction also depends upon the nature of the hydrogen atom undergoing replacement by bromine. The order of reactivity is tertiary > secondary > primary.

As a result of their study of the effect of light, oxygen, and inhibitors on the bromination of naphthenes, Kharasch and co-workers [31, 1941] suggested a chain mechanism involving the formation of bromine atoms.

(1) $Br_2+\nu \longrightarrow 2\,Br$

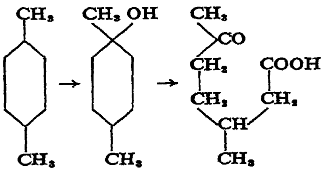
(2) $R{-}H+Br \longrightarrow R+HBr$

(3) $R+Br_2 \longrightarrow RBr+Br$

The Oxidation of Naphthenes

Naphthene hydrocarbons react slowly with oxygen at room temperature to give various liquid oxygenated products together with gaseous oxidation products. The reaction probably proceeds via the intermediate formation of a hydroperoxide and results in the formation of cyclic oxygenated compounds such as alcohols and ketones together with compounds in which the naphthene ring has been ruptured.

Chavanne and co-workers [9, 12, 1931; 7, 10, 1930; 8, 1932] have studied the absorption of oxygen by various naphthenes at room temperature and at 100°. It was found that whereas 1,2-, 1,3-, and 1,4-dimethylcyclohexanes reacted under these conditions and absorbed all the oxygen present, hydrocarbons such as 1,1-dimethylcyclopentane and 1,1-dimethylcyclohexane were inert towards oxygen. It would thus appear that a tertiary hydrogen atom is necessary for ease of oxidation. Examination of the reaction products confirms that such hydrogen atoms are, in fact, the site of reaction. Thus Chavanne and Bode [7, 1930] isolated 1,4-dimethylcyclohexanol-1 and β-methyl-δ-acetyl valeric acid from the oxidation of 1,4-dimethylcyclohexane.



β-methyl-δ-acetyl valeric acid.

Analogous products were obtained from other alkylnaphthenes such as 1,3-dimethylcyclopentane and ethyl- and butyl-cyclopentane [Chavanne, 11, 1931; Dupont, 19, 1933].

The possibility of the liquid-phase oxidation of naphthenes has resulted in the development of processes for the oxidation of cyclohexane to adipic acid, which is used in the manufacture of nylon. Cavanaugh and Nagle [6, 1944] describe the oxidation of cyclohexane to adipic acid by means of nitric acid of strength 45–75% at 100–200° C. and under 2–10 atm. pressure. Nitrocyclohexane is also obtained in this reaction. The formation of adipic acid by the catalytic oxidation of cyclohexane with oxygen in the liquid phase at a temperature of 60° C. is described by Loder [33, 1940]. The catalyst used was an acetate of cobalt, copper, or manganese.

In some processes, cyclohexane is not oxidized directly to adipic acid but reaction conditions are arranged so that the products are cyclohexanol and cyclohexanone. Such a process is described by Loder [34, 1940], who states that the oxidation is carried out in the liquid phase with an oxygen-containing gas at a temperature of 100–250° C. in the presence of an oxidation catalyst. The cyclohexanol and cyclohexanone are subsequently oxidized to adipic acid.

The ignition and cool flame characteristics of the combustion of cyclohexane have been studied by Burgoyne [5, 1940], and it was found that this hydrocarbon behaves in a similar manner to paraffin hydrocarbons such as *n*-hexane. Chowdhury and Saboor [18, 1937] oxidized cyclohexane in the vapour phase with oxygen using a tin vanadate catalyst. The products contained acetaldehyde, acrolein, and acetic and pyruvic acids together with unsaturated hydrocarbons and peroxides. It was found that the formation of acids and peroxides was favoured at 250–340° C., whereas at 350–420° C. the formation of aldehydes and unsaturated compounds predominated.

The use of solid catalysts in the vapour-phase oxidation of hydrocarbons often causes considerable breakdown of the products because of the formation of local 'hot spots' on the catalyst. The use of gaseous catalysts has therefore been studied and hydrogen bromide is the most successful yet tried. In the presence of such a catalyst, reaction takes place at a much lower temperature, thus giving less chance of breakdown of the products. Rust and Vaughan [39, 1945] describe the formation of cyclohexanone from cyclohexane and of cyclopentanone from cyclopentane. The hydrocarbon together with oxygen, hydrogen bromide, and an inert diluent such as nitrogen or steam is passed through a reactor at a temperature of about 200° C. With a reaction time of about 6 minutes, 45% of the introduced oxygen is found in the reaction products.

The Dehydrogenation of Naphthenes

Naphthenes such as cyclohexane may be dehydrogenated to aromatic hydrocarbons by passage over a suitable catalyst. Balandin and Kotelkov [3, 1942] studied the dehydrogenation of cyclohexane over various catalysts in the temperature range 300–600° C. With a platinized-nichrome catalyst it was found that dehydrogenation took place up to 400° C., but at higher temperatures cyclohexane was thermally decomposed to carbon, hydrogen, and methane.

Balandin [2, 1942] carried out a kinetic study of the dehydrogenation of cyclohexane over various copper-chromium oxide catalysts in the temperature range 380–530° C. With a copper-chromium oxide catalyst using Cr_2O_3 prepared from $Cr_2(CrO_3)_3$, formation of unsaturated compounds was observed. The proportion of unsaturated hydrocarbon formed decreased with increasing temperature owing to the reaction series:

cyclohexane → cyclohexene → cyclohexadiene → benzene.

Platinized charcoal is also a dehydrogenation catalyst and it has been used for the dehydrogenation at about 300° of the products of naphthene isomerization. The aromatic hydrocarbons thus produced serve to identify the naphthenic products of the isomerization.

Catalysts using alumina as a support for the oxides of other metals such as molybdenum or vanadium are the most commonly used catalysts for the dehydrogenation of naphthenes. Thus Grosse [21, 1943] describes a reaction suitable for the conversion of methylcyclohexane to toluene in which the contact catalyst is gamma alumina supporting an oxide of vanadium, columbium, or tantalum. The reaction is carried out at a temperature of about 500° C. and under a pressure of 4–100 lb. per sq. in. Meier [35, 1945] describes the dehydrogenation of naphthene fractions in the presence of hydrogen at about 500° C. under a pressure of 200 lb. per sq. in. over an Al_2O_3—MoO_2 catalyst.

Hydrogen is usually present during the reaction in order to prevent excessive deposition of carbon on the catalyst and consequent loss of activity. The supported metal oxide catalysts are usually preferable to metallic catalysts since they are less susceptible to poisoning than the latter.

Hydrogenation of Naphthenes

When naphthenes are reduced with hydrogen over a catalyst, rupture of the ring takes place and a mixture of normal and isoparaffins is obtained. Thus Kazanskiĭ and co-workers [26, 1939] found that butylcyclopentane broke down to form a mixture of hydrocarbons including 4-methyloctane when passed over nickel deposited on alumina at 250° C. in the presence of hydrogen. It was further found that isoamylcyclopentane when passed over nickel or platinized carbon in a nitrogen stream gave 38% of aromatic hydrocarbons. In a hydrogen stream, however, 2,5-dimethyloctane was formed. Similar formation of paraffins from ethyl- and propylcyclopentane at 300° C. over platinized carbon was also observed by Kazanskiĭ [27, 1941]. It was found that, with an active catalyst, both of these naphthenes gave different paraffin hydrocarbons but an exhausted catalyst resulted in the formation of very similar products in both cases. In both reactions, however, the major proportion of the products consisted of isoparaffins.

Nikolaeva [37, 1942] obtained *n*-hexane, isohexane, and cyclohexane by passing methylcyclopentane over a molybdenum sulphide catalyst at 400° C. and under a hydrogen pressure of 400 atm. Cyclohexane under similar conditions gave 34% of isomeric hexanes and 62% methylcyclopentane. The results of this work indicate that the paraffinic hydrocarbons are formed from methylcyclopentane produced by isomerization of the cyclohexane and not by direct breaking of the cyclohexane ring.

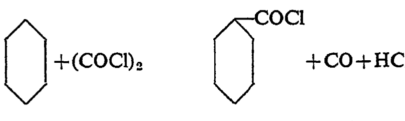
Isomerization of Naphthenes

In the presence of aluminium chloride, naphthenes isomerize to form equilibrium mixtures of naphthenic hydrocarbons. Thus cyclohexane isomerizes to methylcyclopentane under these conditions and at 25° C. the equilibrium mixture contains about 12% of methylcyclopentane [Glasebrook and Lovell, 20, 1939]. The proportion of methylcyclopentane increases with increasing temperature and reaches 25·6% at 77·4° C. At higher temperatures aluminium chloride is unsatisfactory as a catalyst since undesirable side reactions take place. Pure dry aluminium chloride is inert towards naphthenes and the presence of moisture or of hydrogen chloride is necessary in order to effect isomerization. Molybdenum sulphide has also been used as a catalyst for the isomerization of cyclohexane, and Andō [1, 1939] reports that at 400° C. and under a pressure of 200 atm., cyclohexane gives methylcyclopentane as the main product. At a flow rate of 113 ml. per hour and a temperature of 411° C., the product contained 79·4% methylcyclopentane.

The isomerization of methylcycloheptane over aluminium chloride was studied by Turova-Pollak [41, 1943], who found that the product on dehydrogenation gave chiefly *p*-xylene. The isomerization product was therefore 1,4-dimethylcyclohexane. Similarly it was found by the same author [42, 43, 1941] that both cycloheptane and 1,2-dimethylcyclopentane gave chiefly methylcyclohexane when isomerized in the presence of aluminium chloride. Hexahydromesitylene, however, showed no change after reaction with aluminium chloride.

The Carboxylation of Naphthenes

Kharasch and Brown [29, 1940; 30, 1942] have studied the reaction between naphthenes, such as cyclohexane, and oxalyl chloride. It was found that when the reaction mixture was irradiated with ultra-violet light at reflux temperature, reaction took place to give good yields of naphthenic acid chlorides. The gaseous products were carbon monoxide and hydrogen chloride



The same reaction takes place in the absence of light if in the presence of organic peroxides such as benzoyl peroxide.

The reaction may also be carried out by using phosgene instead of oxalyl chloride.

Under conditions of catalysis both by light and by peroxides the reaction is said to proceed by means of a chain involving chlorine atoms and free alkyl radicals. In the case of the peroxide catalysed reaction, the chain length appears to be rather short since about 5 mole % of benzoyl peroxide is required.

The Reaction of Naphthenes with Sulphuryl Chloride

Kharasch and Read [32, 1939] investigated the reaction between sulphuryl chloride and cyclohexane and found that both sulphonation and chlorination took place. The relative amounts of cyclohexylsulphonyl chloride and cyclohexyl chloride formed in this reaction depend chiefly upon the catalyst used. Peroxide catalysts give chlorination exclusively, while mercaptan catalysts give only relatively small amounts of sulphonation even under optimum conditions. Anthraquinone sulphonic acids were found to initiate the reaction in the light but they were without effect in the dark. These catalysts again gave far more chlorination than sulphonation.

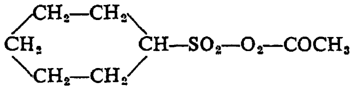
The most effective catalysts for sulphonation were found to be cyclic nitrogenous compounds such as pyridine and quinoline. The reaction mixture was irradiated and the sulphuryl chloride added drop-wise to the hydrocarbon. Yields of about 40% cyclohexyl sulphonyl chloride were obtained together with about 20% of cyclohexyl chloride. Similar results were obtained with methylcyclohexane.

The Sulphoxidation of Cyclohexane

'Hostapon' Process.

As a result of their war-time researches into the production of detergents the Germans found that sulphonic acids of saturated hydrocarbons could be prepared by the direct reaction of the hydrocarbon with gaseous sulphur dioxide and oxygen. The process [4, 1946] was carried out in the presence of acetic anhydride and it was found necessary to irradiate the reactants with ultra-violet light in order to initiate the reaction. A similar result was obtained by using ozonized oxygen instead of ultra-violet light or by replacing the acetic anhydride by acetyl chloride or by the use of gaseous keten. Other methods of initiating the reaction include the addition of 30% hydrogen peroxide to the hydrocarbon-acetic anhydride mixture or simply by heating the reactants to 70° C. while passing the mixture of sulphur dioxide and oxygen. This last method depends upon the initial formation of a hydrocarbon oxidation product which initiates the sulphoxidation reaction.

The first product is a mixed per-anhydride of cyclohexane sulphonic acid and acetic acid, a compound which was isolated in a crystalline form:



This can then decompose in various ways to give cyclohexane sulphonic acid.

(*a*) Thermal decomposition in a hydrocarbon solvent:
$C_6H_{11}SO_2—O_2—COCH_3 \rightarrow C_6H_{11}SO_3H +$ decomposition products

(*b*) $C_6H_{11}SO_2—O_2—COCH_3 + SO_2 \xrightarrow{50–60^\circ} 2C_6H_{11}SO_3H$ + decomposition products

(*c*) $6C_6H_{12} + 6SO_2 + \frac{5}{2}O_2 + C_6H_{11}—SO_2—O_2—COCH_3$
$\rightarrow 7C_6H_{11}SO_3H +$ decomposition products

(*d*) $C_6H_{11}SO_2—O_2—COCH_3 + SO_2 + 2H_2O$
$\rightarrow C_6H_{11}SO_3H + H_2SO_4 + CH_3COCH$

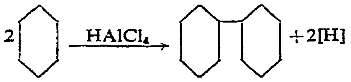
(*e*) $6C_6H_{12} + 6SO_2 + \frac{5}{2}O_2 + C_6H_{11}SO_2—O_2—COCH_3 + H_2O$
$\rightarrow 7C_6H_{11}SO_3H + CH_3COOH.$

It will be observed that these reactions do not balance. They are quoted in the report on the German process together with the statement, in the case of reaction (*e*), that the amount of sulphonic acid produced is about 7–9 times the amount of the reacting per-anhydride.

The Alkylation of Naphthenes

In the presence of aluminium chloride and hydrogen chloride, naphthenes react with olefines to form alkyl naphthenes. Owing to the isomerizing influence of the catalyst, the products of the reaction are often mixtures of hydrocarbons. Pines and Ipatieff [38, 1941] studied the alkylation of cyclohexane and methylcyclohexane with olefines such as propene and normal and isobutene and found that methylcyclohexane reacted more readily than cyclohexane. It was also found that the methyl group in methylcyclohexane stabilized the simple alkylation product since this was the chief product of the reaction. With cyclohexane, however, a considerable amount of isomerization took place and 1,3,5-trimethylcyclohexane was obtained in the reaction with propene.

The reaction products are further complicated by side reactions involving dehydrogenation of the naphthene to form cyclic olefines. These unsaturated compounds combined with the aluminium chloride catalyst, from which they could be liberated by the addition of water. Other dehydrogenation reactions involved the formation of dicyclohexyl from 2 molecules of cyclohexane. The hydrogen liberated in these reactions served to reduce the olefines to paraffins which were identified in the reaction gases.



$$CH_3—CH{=}CH_2+2[H] \rightarrow CH_3—CH_2—CH_3.$$

The relative amount of this intermolecular dehydrogenation-hydrogenation reaction increases with increase in reaction temperature.

Sulphuric acid may also be used as a catalyst, and Ipatieff and Pines [24, 1943] describe the production of *p*-methyl-*tert*-butylcyclohexane from the reaction between isobutene and methylcyclohexane under these conditions.

Isomerization of the ring structure also takes place during the alkylation reaction between propene or butene and methylcyclopentane in the presence of a catalyst such as sulphuric acid, boron trifluoride, or hydrogen fluoride [22, 1942; 23, 1943; 25, 1944]. In these reactions isomerization of the simple alkylation product takes place since 1-ethyl-2,4-dimethylcyclohexane is claimed as the product of reaction between methylcyclopentane and *n*-butene.

REFERENCES

1. Andō, S. *J. Soc. Chem. Ind. Japan*, **42**, Suppl. binding, 322 (1939).
2. Balandin, A. A., and Kostin, F. L. *Acta Physicochim. U.R.S.S.* **17**, 211 (1942).
3. Balandin, A. A., and Kotelkov, N. Z. *Bull. Acad. Sci. U.R.S.S., Classe Sci. Chim.* 230 (1942).
4. B.I.O.S. Final Report No. 478 *Textile Auxiliary Products. Development of Mersol and Hostapon processes by I.G. Farbenindustrie, Hochst.* H.M. Stationery Office, London (1946).
5. Burgoyne, J. H., Tang, T. L., and Newitt, D. M. *Proc. Roy. Soc.* (*London*), A **174**, 379 (1940).
6. Cavanaugh, R. M., and Nagle, W. M. U.S. Pat. 2,343,534 (7 Mar. 1944).
7. Chavanne, G., and Bode, E. *J. Am. Chem. Soc.* **52**, 1609 (1930).
8. Chavanne, G., Katzenstein, and Pahlavouni. *Bull. Soc. Chim. Belg.* **41**, 209 (1932).
9. ——— ——— ——— *Bull. Soc. Chim. Belg.* **40**, 626 (1931).
10. Chavanne, G., and Miller, O. *Bull. Soc. Chim. Belg.* **39**, 287 (1930).
11. ——— ——— *Bull. Soc. Chim. Belg.* **40**, 611 (1931).
12. Chavanne, G., Miller, O., and Cornet. *Bull. Soc. Chim. Belg.* **40**, 673 (1931).
13. Chiurdoglu, G. *Bull. Soc. Chim. Belg.* **41**, 152 (1932).
14. ——— *Bull. Soc. Chim. Belg.* **42**, 347 (1933).
15. ——— *Bull. Soc. Chim. Belg.* **43**, 35 (1934).
16. ——— *Bull. Soc. Chim. Belg.* **47**, 363 (1938).
17. ——— *Bull. Soc. Chim. Belg.* **53**, 45 (1944).
18. Chowdhury, J. K., and Saboor, M. A. *J. Indian Chem. Soc.* **14**, 638 (1937).
19. Dupont, P., and Chavanne, G. *Bull. Soc. Chim. Belg.* **42**, 537 (1933).
20. Glasebrook, A. L., and Lovell, W. G. *J. Am. Chem. Soc.* **61**, 1717 (1939).
21. Grosse, A. V., and Mattox, W. J. U.S. Pat. 2,319,452 (18 May 1943).
22. Ipatieff, V. N., and Pines, H. U.S. Pat. 2,291,254 (28 July 1942).
23. ——— ——— U.S. Pat. 2,315,078 (30 Mar. 1943).
24. ——— ——— U.S. Pat. 2,334,099 (9 Nov. 1943).
25. ——— ——— U.S. Pat. 2,340,537 (1 Feb. 1944).
26. Kazanskiĭ, B. A., and Sergienko, S. R. *J. Gen. Chem.* (*U.S.S.R.*), **9**, 447 (1939).
27. Kazanskiĭ, B. A., Solovova, O. P., and Bashulin, P. A. *Bull. Acad. Sci. U.R.S.S., Classe Sci. Chim.* 107 (1941).
28. Kharasch, M. S., and Berkman, G. *J. Org. Chem.* **6**, 810 (1941).
29. Kharasch, M. S., and Brown, H. C. *J. Am. Chem. Soc.* **62**, 454 (1940).
30. ——— ——— *J. Am. Chem. Soc.* **64**, 329 (1942).
31. Kharasch, M. S., Hered, W., and Mayo, F. R. *J. Org. Chem.* **6**, 818 (1941).
32. Kharasch, M. S., and Read, A. T. *J. Am. Chem. Soc.* **61**, 3089 (1939).
33. Loder, D. J. U.S. Pat. 2,223,493 (3 Dec. 1940).
34. ——— U.S. Pat. 2,223,494 (3 Dec. 1940).
35. Meier, H. H. U.S. Pat. 2,375,573 (8 May 1945).
36. Mousseron, M., and Granger, R. *Compt. rend.* **207**, 366 (1938).
37. Nikolaeva, A. F. *J. Gen. Chem.* (*U.S.S.R.*), **12**, 240 (1942).
38. Pines, H., and Ipatieff, V. N. *J. Org. Chem.* **6**, 242 (1941).
39. Rust, F. F., and Vaughan, W. E. U.S. Pat. 2,369,181 (13 Feb. 1945).
40. Thorpe, J. F., and Farmer, E. H. *The Science of Petroleum*, vol. **2**, 969 (1938).
41. Turova-Pollak, M. B., and Rappoport, P. L. *J. Gen. Chem.* (*U.S.S.R.*), **13**, 353 (1943).
42. Turova-Pollak, M. B., and Sidel' Kovskaya, F. P. *J. Gen. Chem.* (*U.S.S.R.*), **11**, 817 (1941).
43. Turova-Pollak, M. B., and Vsevolozhskaya, E. V. *J. Gen. Chem.* (*U.S.S.R.*), **11**, 824 (1941).
44. Zelinsky, N. *Ber.* **35**, 2677 (1902).

THE CHEMISTRY OF AROMATIC HYDROCARBONS

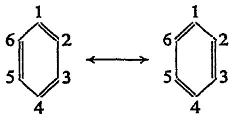
By **W. J. OLDHAM**

Anglo-Iranian Oil Co. Ltd.

THE presence of the benzene nucleus in hydrocarbons endows these compounds with chemical properties different from those of either the paraffin or olefine hydrocarbons. A brief discussion of the general nature of the benzene molecule will therefore be of use in a study of its chemical properties.

The most common and important chemical reactions of benzene are those in which nuclear hydrogen atoms are replaced by other elements, and it has long been recognized that the structure suggested for benzene by Kekulé does not satisfactorily explain all of these observed properties. The stability of the benzene molecule is greater than that of a simple Kekulé molecule, which contains three double bonds, and approaches that of the paraffin hydrocarbons. It has also been shown that the distances between all six carbon atoms in benzene are identical and equal to 1·39 Å. A molecule of the Kekulé type would be expected to possess single bonds of length 1·54 Å and double bonds of length 1·35 Å.

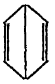
The concept of resonance has provided an explanation of the stability and symmetry of benzene and this compound may be considered to be in a state of resonance between the two possible Kekulé forms:



According to this concept the electrons in the benzene molecule have more freedom than is indicated by the Kekulé structure and will arrange themselves in the configuration intermediate between the two forms, corresponding to the least energy. Since the two limiting structures are identical they make equal contributions to the resonance structure which will therefore be symmetrical.

It is found that the observed heat of formation of benzene exceeds the value calculated for the Kekulé structure by 39 kg.-cal. per mole. This value is called the resonance energy and gives a measure of the stability of benzene compared with that of the cyclohexatriene structure of Kekulé.

The observed stability and symmetry of benzene may thus be accounted for by the concept of resonance between the two Kekulé structures. More accurate treatment of the problem involves consideration of the resonance contributions of other possible benzene structures such as that suggested by Dewar.



Dewar structure.

Substitution in the nucleus of a monoalkylaromatic hydrocarbon takes place chiefly in the ortho- and para-positions. This may be accounted for by the fact that the alkyl group, being electron repelling, loses electrons to the aromatic ring, thereby increasing the electron density at the ortho- and para-positions and giving rise to a molecule with increased activity towards electrophilic substituents at these points. This increased reactivity of alkylaromatic hydrocarbons, in which the symmetry and stability of the benzene molecule is disturbed, is observed in many of the reactions described below.

The Nitration of Aromatic Hydrocarbons

The nitration of aromatic hydrocarbons is carried out with nitric acid either alone or with sulphuric acid or with a mixture of acetic acid and anhydride. With increasing temperatures and higher nitric acid concentrations, the yield of polynitro compounds increases. As a rule, the alkylated aromatic hydrocarbons are more readily nitrated than is benzene itself.

Ingold *et al.* [29, 1931] have studied the nitration of toluene with nitric acid in the liquid phase in order to determine the relative amounts of isomers formed. The values obtained were 59% ortho, 4% meta, and 37% para nitrotoluene. Bullock and Mitchell [7, 1941, 1943] have studied the vapour-phase nitration of toluene over a temperature range of 150–250° C. with concentrations of nitric acid from 70 to 90%. They found that the ratio of the isomers in the product varied very little over this wide range of reaction conditions. The values obtained at 150° C. with 70% HNO_3 were 55·8% ortho, 5·0% meta, and 39·2% para nitrotoluene.

During some nitration reactions, dealkylation occurs. Doumani and Kobe [14, 1942] have shown that the formation of some *p*-nitrotoluene during the nitration of *p*-cymene is due to the direct replacement of the isopropyl group by the nitro group. Acetone and isopropanol are found in the reaction mixture and are undoubtedly formed by the oxidation of the displaced isopropyl group.

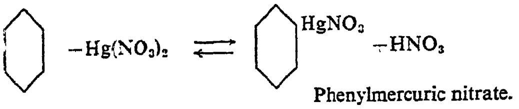
Aromatic hydrocarbons can also be nitrated with nitrogen dioxide. Thus Titov and Baeryshnikova [74, 1940; 75, 1936] nitrated benzene with nitrogen dioxide in sulphuric acid and obtained nitrobenzene in 98·4% yield. Toluene under similar conditions gave a mixture of nitrotoluenes. In the absence of the sulphuric acid the nitration takes place in the methyl group of toluene and phenylnitromethane is formed. The same product results if toluene is nitrated with nitric acid under pressure. Titov [74, 1940] showed that pure nitric acid nitrates only in the ring, but if nitric oxide is present nitrogen dioxide is formed and the side chains are also nitrated. Benzene has also been nitrated in the vapour phase with nitrogen dioxide under the influence of ultra-violet light to give nitrobenzene, *m*-dinitrobenzene, and trinitrophenols [Avanesov, 2, 1939]. It would appear, however, that the use of nitrogen dioxide offers no advantages over the classical method of nitration using nitric and sulphuric acid mixtures.

Nitration is also possible by electrochemical means. Good yields of the nitro compounds of xylene and toluene may be obtained in this way, but Atanasin reports that benzene gives chiefly oxidation products [1, 1937–8].

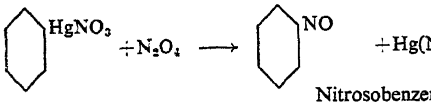
The Oxynitration of Benzene.

Nitro phenols may be produced directly from benzene by the action of a solution of mercuric nitrate in nitric acid.

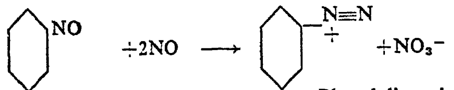
During the war this reaction was the subject of a considerable amount of study and the overall yield on the conversion of benzene to dinitrophenol was increased to about 85%. Westheimer, Carmack, *et al.* [78, 1947] have studied the mechanism of the reaction and have shown that phenyl mercuric nitrate, nitrosobenzene, and phenyl diazonium nitrate are intermediate products in the formation of phenol from benzene. The phenol is then nitrated to give mono- or poly-nitro phenols.


(1)

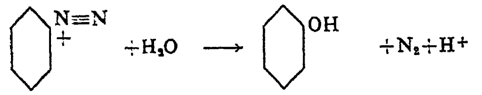
Phenylmercuric nitrate.

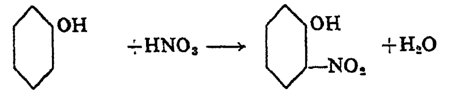

(2)

Nitrosobenzene.

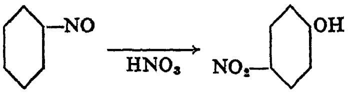

(3)

Phenyl diazonium nitrate.


(4)


(5)

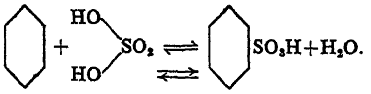
If the nitric acid concentration is high (50%) and the nitrous acid concentration is low, the reaction proceeds by a different route and nitro phenol is produced directly from the nitrosobenzene formed as in equation (2).



The reaction is not limited to benzene, nitro cresols having been prepared by the oxynitration of toluene.

Sulphonation of Aromatic Hydrocarbons

The aromatic nucleus readily reacts with sulphuric acid to form arylsulphonic acids.



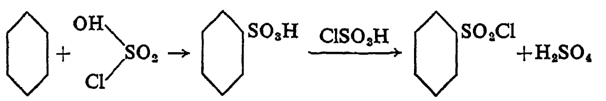
The ease of sulphonation increases with increasing numbers of alkyl substituents in the nucleus. When the number of substituents exceeds three, the product of sulphonation may be contaminated with isomeric sulphonic acids owing to the Jacobsen rearrangement (see below).

The site of sulphonation within the nucleus depends upon the substituents already present and also upon the reaction conditions. Thus toluene gives ortho- and para-toluenesulphonic acids in almost equal quantities at 0° C., whereas at 100° C. the ratio of para- to ortho-sulphonic acid is about 6:1. A small quantity of meta-toluene sulphonic acid is formed in each case. A compound, such as *tert.*-butylbenzene, which contains a large alkyl group, gives no ortho-sulphonic acid, substitution taking place in the para-position.

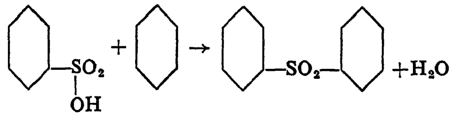
The presence of mercury in the sulphonation reaction can increase the rate of reaction and also influence the site of sulphonation. The most marked example of this effect is in the sulphonation of anthraquinone which normally takes place in the β-position but which takes place exclusively in the α-position in the presence of a small amount of mercury. This effect is not so marked with hydrocarbons but it has been observed with *o*-xylene. Other metal sulphates which catalyse the sulphonation reaction are cadmium, lead, aluminium, and iron.

Sulphonation consists essentially in the addition of sulphur trioxide to the aromatic nucleus and it may in fact be carried out by the direct reaction between the hydrocarbon and sulphur trioxide in a solvent. The solvent is usually sulphuric acid (oleum), but chloroform can also be used. Concentrated sulphuric acid alone may be used for sulphonation, but the reaction is slower and the attainment of equilibrium requires a much greater length of time. In order to obtain complete sulphonation, the water must be removed as it is formed in order to destroy the equilibrium which would otherwise be set up.

Chlorosulphonic acid may also be used as the sulphonating agent, but its use is somewhat limited because it also forms sulphonyl chlorides.



The sulphonation of aromatic hydrocarbons with sulphuric acid can be effectively promoted by the use of hydrogen fluoride. The resultant product is either a sulphonic acid or a symmetrical sulphone formed by further condensation of the initial sulphonic acid. The formation of the sulphone is favoured by a higher temperature [Simons, 68, 1941].



Boron trifluoride has also been used as an effective promoter and dehydrating agent in the sulphonation of aromatic hydrocarbons with sulphuric acid [Thomas, 73, 1940]. Under these conditions naphthalene gives α-naphthalene sulphonic acid as the main product at 30° C., whereas the β-isomer is the predominant product at 160° C.

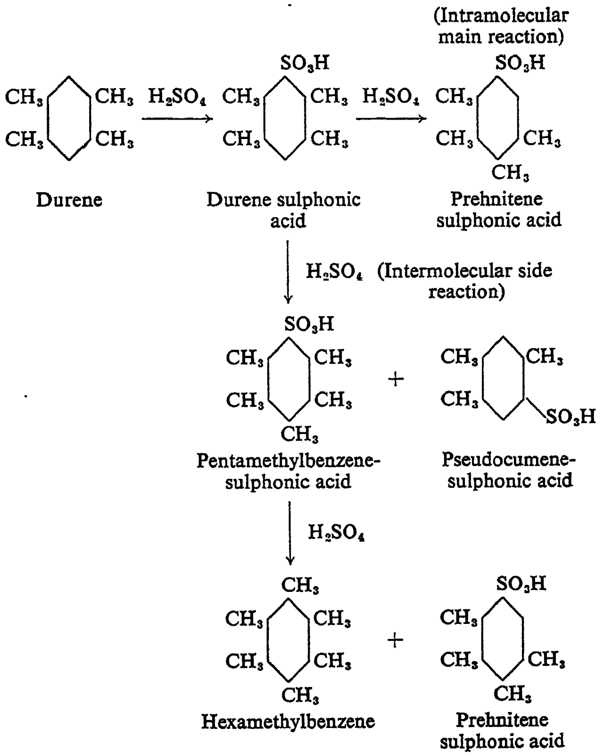
Sulphonic acids undergo hydrolysis when heated with water or dilute acid and the original hydrocarbon may be recovered in this way. The stability of the sulphonic acid towards hydrolysis varies with different compounds and those acids which are more readily formed are the more easily hydrolysed. These differential rates of sulphonation and hydrolysis are made use of in separating hydrocarbons which cannot be conveniently purified by other means. Thus hydrolysis of a mixture of the sulphonic acids of meta- and para-xylene at 120° C. results in hydrolysis of the meta-compound only and the meta-xylene so formed may be removed by steam distillation as the hydrolysis proceeds. When the temperature of hydrolysis is raised to about 140° C. the *p*-xylene sulphonic acid is hydrolysed. Similarly, hydrolysis of a mixture of α- and β-naphthalene sulphonic acids at about 150° C. results in hydrolysis of the α-isomer with little loss of the β-isomer which can then be recovered in a purified form.

Kharasch [37, 1939] has studied the sulphonation of alkylaromatic compounds with sulphuryl chloride. Using a mercaptan-type catalyst and in the presence of strong light he found that sulphonation took place in the aliphatic side chain except in the case of toluene. A free radical mechanism is postulated to explain this reaction of sulphuryl chloride which in the presence of aluminium chloride gives nuclear sulphonation.

The Jacobsen Reaction

When a sulphonic acid derived from a polyalkylbenzene is allowed to stand in contact with concentrated sulphuric acid, the alkyl groups migrate to form vicinal polyalkylbenzenes. This migration may be either within one molecule or from one molecule to another, and under normal reaction conditions both types of migration occur simultaneously. No such rearrangement has been observed in molecules containing less than four alkyl substituents.

The rearrangement of durene sulphonic acid to give products containing vicinal methyl groups will serve to illustrate both intra- and inter-molecular migration.


(Intramolecular main reaction)
SO_3H
SO_3H
CH_3
CH_3
H_2SO_4
H_2SO_4
Durene
Durene sulphonic acid
Prehnitene sulphonic acid
H_2SO_4 (Intermolecular side reaction)
+
Pentamethylbenzene-sulphonic acid
Pseudocumene-sulphonic acid
H_2SO_4
+
Hexamethylbenzene
Prehnitene sulphonic acid

The Jacobsen reaction is not limited to the methyl benzenes but also occurs with the ethylbenzenes. A useful summary of the reaction is given by Smith [71, 1942].

Halogenation of Aromatic Hydrocarbons

The halogenation of aromatic hydrocarbons can give rise to two series of products, namely, compounds with the halogen atoms in the side chains and those with halogen atoms in the nucleus.

Halogen substitution in the nucleus is carried out by reaction between the hydrocarbon and the halogen in the presence of a halogen carrier such as iodine, phosphorus, and iron. The function of the halogen carrier is probably to form an additive compound with the halogen, this additive compound being the actual halogenating agent. Iodine derivatives cannot usually be made by direct substitution unless precautions are taken to remove the hydriodic acid as it is formed.

When halogenation is carried out at an elevated temperature and in strong sunlight, but in the absence of a halogen carrier, the site of halogenation is directed to the α-carbon atom of the side chains. Thus toluene is chlorinated commercially by this method to give a mixture of benzyl and benzal chlorides.

Kharasch and Brown [35, 1939] have investigated the effect of peroxides on the site of chlorination. The reagent used as a source of chlorine was sulphuryl chloride, which in the presence of peroxides can give rise to chlorine atoms. The chlorine atoms thus produced are very active chlorinating agents for side chains, the α-carbon atom being attacked. The overall reaction is:

$$ArH + SO_2Cl_2 \xrightarrow[\text{peroxide}]{} ArCl + SO_2\uparrow + HCl\uparrow$$

Cutter and Brown [12, 1944] give further details of the use of sulphuryl chloride in the separate chlorination of the nucleus and the aromatic side chain. The side chains may be chlorinated by the use of peroxides as described above, but in the presence of aluminium chloride and sulphur monochloride the nucleus is chlorinated.

Reduction of Aromatic Hydrocarbons

Aromatic hydrocarbons can be reduced either partially to a cyclic olefine or diolefine or completely to a naphthene. The reduction may be carried out at atmospheric pressure in the presence of colloidal platinum. Larger-scale reductions are normally carried out under pressure in the presence of finely divided nickel. Thus benzene is rapidly hydrogenated over nickel at about 125° C. under 100 atm. pressure. Toluene and other substituted benzenes require slightly higher temperatures to effect reduction.

Aromatics with unsaturated side chains may be reduced to alkyl aromatics without hydrogenation of the nucleus. Finely divided nickel is used as the catalyst and pressures, and temperatures less than those indicated above for nuclear reduction facilitate the reduction of the side chains only.

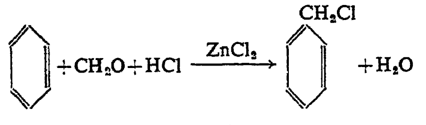
The partial reduction of aromatic hydrocarbons to cyclic olefines such as cyclohexene can be carried out by the decomposition in the hydrocarbon of the ammonia complexes of metals such as calcium, lithium, strontium, and barium. Kazanskii *et al.* [32, 33, 1938; 34, 1937] give details of such experiments and show that benzene can give 90% of cyclohexene together with traces of 1,3-cyclo-hexadiene when allowed to react with the calcium-ammonia complex at room temperature. Reduction does not proceed beyond the cyclohexene stage. With toluene under similar conditions the product was l-methyl cyclohexene-l, the remaining double bond of the nucleus being located at the substituted carbon atom. Reaction of the complexes of lithium and strontium with toluene resulted in the formation of some cyclohexene as by-product, thus indicating that scission of the methyl group had taken place. Naphthalene under these conditions is reduced to tetralin.

Chloromethylation of Aromatic Hydrocarbons

Until about 10 years ago, comparatively little attention had been given to the direct introduction of the chloromethyl group (—CH_2Cl) into the aromatic nucleus, although it was first used by Grassi-Cristaldi and Maselli in 1898 [20, 1898] in a synthesis of benzyl chloride.

This reaction is applicable to most aromatic hydrocarbons and more than one chloromethyl group may be introduced. Benzene, for instance, can give *p*-(dichloromethyl)benzene. Alkyl substituents in the nucleus increase the reactivity of the hydrocarbon towards chloromethylation. Thus toluene, which gives chiefly the parachloromethyl derivative, is about three times as reactive as benzene when chloromethylation is carried out with chloromethyl ether [Vavon, 77, 1939]. Highly reactive compounds such as polymethyl benzenes tend to give large quantities of the diarylmethane derivatives and not the required chloromethyl compounds. These diarylmethane compounds are also formed in large quantities with less reactive hydrocarbons if the reaction time is unduly prolonged. Thus under normal reaction conditions, benzene can give 80% of benzyl chloride and very little diphenylmethane, but with a greatly extended reaction time the yield of diphenylmethane can exceed 50%.

The reaction can be carried out with formaldehyde and hydrochloric acid usually, although not necessarily, in the presence of a condensing agent such as zinc chloride or sulphuric acid.



One of the best methods of chloromethylation is that of Blanc [4, 1923] in which benzene, zinc chloride, and paraformaldehyde are heated to 60° C. and a rapid stream of hydrogen chloride is blown through until no more gas is absorbed. Lock [41, 1941] recommends a slightly lower temperature and a longer reaction time for optimum yields of benzyl chloride.

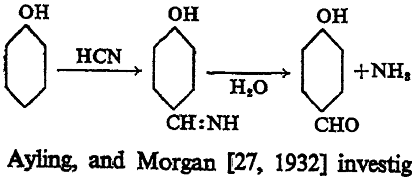
The reaction variables of the chloromethylation of benzene have been studied in some detail on a laboratory and pilot-plant scale by Whitmore, Ginsburg, *et al.* [79, 1946]. The results obtained indicated that benzyl chloride can be prepared in yields of 70% or better and that the zinc chloride catalyst can be regenerated and re-used.

The reaction may also be used for the introduction of bromomethyl and iodomethyl groups and also for groups such as chloroethyl and chloropropyl. The introduction of halogenated alkyl groups into the nucleus of aromatic hydrocarbons produces compounds which are of value in chemical syntheses. An excellent review of the chloromethylation reaction is given by Fuson and McKeever [16, 1942].

The Formation of Aldehydes from Aromatic Hydrocarbons

(a) The Gattermann Reaction.

The Gattermann reaction [17, 1898] was originally used for the production of phenolic aldehydes from phenols, the reagents being hydrogen cyanide, aluminium chloride, and hydrogen chloride. The reaction involves the formation of an aldimine which is subsequently hydrolysed to the aldehyde.



Hinkel, Ayling, and Morgan [27, 1932] investigated the reactivity of aromatic hydrocarbons in this reaction and found that by using temperatures of 100° C. instead of 40° C. or less, as used by Gattermann, good yields of nuclear aldehydes could be obtained from benzene, toluene, and the xylenes. It was found that the yield of aldehyde was increased by using aluminium chloride in excess of the amount required to form the complex $AlCl_3.2HCN$.

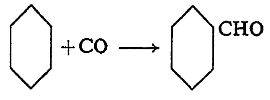
Niedzielski and Nord [50, 1941] subsequently found that, except in the case of benzene, sodium cyanide could effectively and conveniently replace the hydrogen cyanide previously used. It was again found that excess aluminium chloride was essential for good yields and also that the solvent used had a directing influence on the course of the reaction. Thus toluene without a solvent gives a mixture of meta- and para-tolualdehydes, but in the presence of chlorobenzene the para-isomer is obtained exclusively [Niedzielski, 51, 1943].

The presence of aluminium chloride in the reaction mixture has an alkylating influence and often causes the migration of substituent alkyl groups. The products obtained in this reaction are therefore mixtures of alkyl-substituted benzaldehydes.

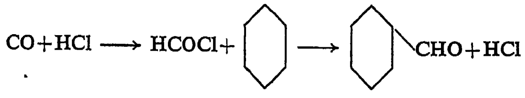
The fact that benzene does not react when sodium cyanide is used, and also that *p*-xylene first undergoes rearrangement to *m*-xylene before reaction, indicates that some polarity in the hydrocarbon molecule is essential for this reaction and it is in fact found that the yield of aldehyde increases with increasing polarity of the hydrocarbons, being greatest with ortho-isomers.

(b) The Gattermann–Koch Reaction.

Carbon monoxide will react with aromatic hydrocarbons under the conditions of the Gattermann–Koch [18, 1897] synthesis to give nuclear aldehydes.



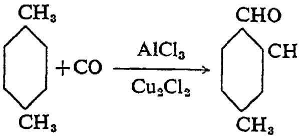
The reaction is promoted by aluminium chloride in the presence of a small quantity of hydrogen chloride or water and an activating agent such as cuprous chloride. Hey [26, 1935] gives details of the formation of benzaldehyde from benzene by passing a stream of carbon monoxide and hydrogen chloride through benzene containing aluminium chloride at a temperature of 45° C. The reaction may be considered as a Friedel–Crafts type of reaction between formyl chloride and the aromatic hydrocarbon.



Activating agents such as the chlorides of titanium and nickel may be used instead of cuprous chloride.

Holloway and Krase [28, 1933] have studied the factors governing the formation of benzaldehyde at temperatures of 25°, 35°, and 50° C. and a pressure of 1,000 lb. per sq. in. It was found that small amounts of water were necessary unless hydrogen chloride was present and that the ratio of aluminium chloride to benzene affected the rate of conversion and the yield. Demann, Krebs, and Borchers [13, 1938] found that 50% of the benzene was converted to benzaldehyde when a 2:1 mixture of benzene and aluminium chloride was heated for 4–8 hours at 30° C. under a carbon monoxide pressure of 70–150 atm.

Alkylated aromatic hydrocarbons react more readily than benzene itself. With disubstituted hydrocarbons the product may be contaminated with isomeric aldehydes owing to the isomerizing effect of the aluminium chloride. Thus *p*-xylene gives 2,4-dimethylbenzaldehyde and not 2,5-dimethylbenzaldehyde.



The Reaction between Benzene and Phosgene

Rueggeberg *et al.* [60, 1946] have investigated the reaction between benzene and phosgene in the presence of aluminium chloride, in order to determine the optimum conditions for the production of benzoic acid. Previous work [Wilson, 80, 1922] had indicated that carbon disulphide was essential as a solvent since the initial complex formed was insoluble in the reaction mixture and was hence prevented from undergoing further reaction with benzene to form benzophenone.

$$C_6H_6 + COCl_2AlCl_3 \rightarrow C_6H_5COCl.AlCl_3 + HCl.$$

Rueggeberg, however, found that excess liquid phosgene could replace the carbon disulphide and that various undesirable sulphur containing by-products could thereby be eliminated.

Benzoic acid is obtained together with varying amounts of benzophenone, by hydrolysis of the aluminium chloride complex. A maximum yield of 55–8 % of benzoic acid was obtained after 16–18 hours' reaction at 3–8° C. using a molar ratio of phosgene to benzene to aluminium chloride equal to 3 to 1 to 1.

This reaction may also be used to produce good yields of symmetrical diaryl ketones by suitable choice of reaction conditions. Excess of the aromatic hydrocarbon is used and fulfils the function of both reactant and solvent. The complex formed as described above reacts with more hydrocarbon to form the ketone.

This method of preparing benzoic acid has the advantage of giving a product free from nuclear chlorine. It is thus superior in this respect to benzoic acid produced by the chlorination of toluene.

The Metalation of Aromatic Hydrocarbons.

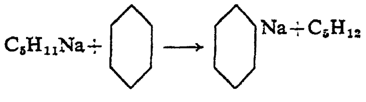
The hydrogen atoms of aromatic hydrocarbons are capable of replacement by metallic atoms such as sodium, potassium, and mercury. These metallic compounds may be formed directly from the hydrocarbon and a suitable compound of the metal concerned.

Kobe and co-workers [38, 1944; 39, 1941; 40, 1942] have described and discussed the mercuration of many aromatic compounds. The number of hydrogen atoms replaceable by mercury may be more than one, and the relative amounts of mono- and poly-compounds formed depends upon the reaction conditions and the reactivity of the hydrocarbon concerned.

Mercuration may be effected by heating the hydrocarbon with either mercuric acetate or the equivalent amount of mercuric oxide in glacial acetic acid at temperatures ranging from 90° to 160° C. The reaction may be written:

$$ArH + Hg(OOCCH_3)_2 \rightarrow ArHgOOCCH_3 + CH_3COOH.$$

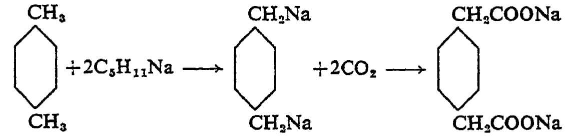
Morton and co-workers [46, 1943] describe the formation of sodium derivatives of aromatic hydrocarbons by heating the hydrocarbon with sodium amyl.



The disodium compounds formed are meta-isomers. Toluene and the xylenes give compounds in which the sodium is substituted in the methyl groups. *o*-Xylene also gives some substitution in the nucleus.

Carboxylic acids are formed when the sodium compounds are decomposed by pouring on to solid carbon dioxide and these acids serve to indicate the site of metalation in the hydrocarbon.

Thus benzene gives rise to benzoic and isophthalic acids. Toluene gives phenylacetic and homo-isophthalic acids and the xylenes give phenylene diacetic acids. *p*-Xylene was also found to give some *p*-tolylacetic acid.



These metallic compounds are considered to be intermediate compounds in the alkylation reaction between an aromatic hydrocarbon and an alkyl halide in the presence of sodium metal (Morton *et al.*, loc. cit.).

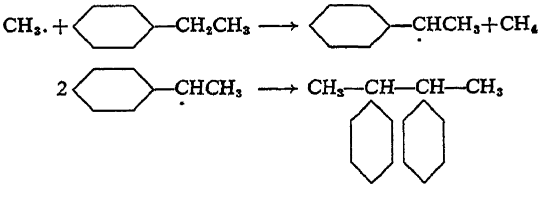
Thus methylhexylbenzenes were obtained by dropping amyl chloride on to sodium in hot xylene, substitution by the amyl group taking place in one of the methyl groups of the xylene molecule. The reactivity of the xylenes varies between the three isomers and the yields obtained were:

p-Xylene . . .	54%
m-Xylene . . .	32%
o-Xylene . . .	22%

The Reaction of Alkyl Aromatic Hydrocarbons with Free Methyl Radicals

The reactivity of the α-hydrogen atoms in alkylaromatic hydrocarbons is illustrated by the work of Kharasch [36, 1945] on the reactions of free methyl radicals. It was found that the latter, formed by the thermal decomposition of diacetyl peroxide in aromatic hydrocarbons, abstracted the α-hydrogen atoms of the hydrocarbon to form methane and that two of the aromatic radicals thus produced combined to give good yields of the dimer.

Thus with ethylbenzene:



The reaction then continues with the α-hydrogen atoms of the dimer to give some trimer and tetramer. With isopropylbenzene, however, no trimer or tetramer is formed because the dimer contains no α-hydrogen atoms. This reaction may prove to be of some value in the preparation of higher aromatic hydrocarbons in the laboratory.

Oxidation of Aromatic Hydrocarbons

Aromatic hydrocarbons may be oxidized either in the side chain or in the nucleus. Nuclear oxidation may involve either rupture of the ring or oxygen addition as in the formation of phenols. In general, with the simple alkyl-aromatic hydrocarbons, the side chains are more readily oxidized than the nucleus, the point of oxygen attack usually being on the side-chain carbon atom adjacent to the nucleus.

Various reagents may be used in the oxidation of aromatic hydrocarbons and the following methods are those most generally used:

1. Potassium permanganate may be used to oxidize the side chains of aromatic hydrocarbons, the product being a nuclear carboxylic acid. Thus toluene gives benzoic acid and *o*-xylene is oxidized to phthalic acid. This reagent will slowly oxidize the aromatic nucleus to a mixture of formic and oxalic acids.
2. Dilute nitric acid is a very useful reagent for the successive oxidation of side chains in a polyalkyl aromatic hydrocarbon. In general, the longest side chain is preferentially oxidized to a carboxyl group.
3. Chromic acid is a more powerful oxidizing agent and will convert all of the side chains into carboxyl groups. Some aromatic hydrocarbons are completely decomposed into carbon dioxide and water with this reagent.
4. Chromyl chloride (CrO_2Cl_2) is useful for reactions such as the partial oxidation of toluene to benzaldehyde. Manganese dioxide either alone or with sulphuric acid may also be used.
5. The chemical oxidation of benzene to phenol has not met with much success, but some experiments have been carried out using hydrogen peroxide in the presence of a catalyst such as vanadium pentoxide. Under these conditions Milas [45, 1937] obtained a 30% yield of phenol from benzene.

Oxidation with Gaseous Oxygen.

The direct oxidation of aromatic hydrocarbons by oxygen, with or without the aid of catalysts, has been the subject of a great amount of research and many claims are to be found in the patent literature. The ignition and cool flame characteristics of benzene and the alkyl aromatic hydrocarbons have been investigated in some detail by Newitt and Burgoyne [9, 1936; 8, 10, 1940]. The kinetics of the reaction and the distribution of oxygen in the products were also investigated.

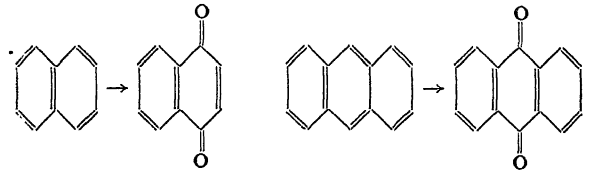
(a) Oxidation Involving Rupture of the Nucleus. The most important reactions of this type are the oxidation of benzene to maleic anhydride and of naphthalene to phthalic anhydride. Many processes have been described, but the most successful is the vapour-phase oxidation of the hydrocarbon at about 400° C. using vanadium pentoxide on a support such as silica gel as a catalyst. Air is used as the oxidant and yields of upwards of 50% are obtainable.

(b) Oxidation of the Nucleus. The oxidation of benzene to phenol has received a great deal of attention, but the yields, where reported, are not very large. Some patents recommend pressures of about 50 atm. for a non-catalytic oxidation at 200° C. to 400° C. [Bone, 5, 1940], whereas other processes use a catalyst such as fused boron oxide and a temperature of 750–800° C. [Moyer, 47, 1943].

Harman [25, 1945] describes the oxidation of benzene to phenol with air in the presence of 0·02% by volume of iodine vapour. The reaction temperature is 604° C. and the yield is 68 lb. of phenol per 100 lb. of treated benzene. The reaction is also applicable to toluene and naphthalene.

The liquid-phase oxidation of benzene with molecular oxygen in anhydrous hydrofluoric acid has recently been reported [Simons, 65, 1946]. Temperatures of less than 200° C. are used and the yield of phenol from benzene is 100% although the conversion is considerably less. Toluene is oxidized to orthocresol in preference to benzoic acid, and it would appear that hydrofluoric acid may be a useful solvent for obtaining nuclear oxidation in preference to oxidation of the side chains.

The nuclear oxidation of naphthalene and anthracene can be carried out in the vapour phase to give naphthaquinone and anthraquinone respectively.



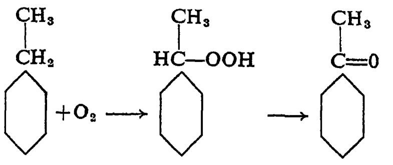
Naphthaquinone, on further oxidation, will of course give phthalic anhydride as described above and it is probably an intermediate product formed during the oxidation of naphthalene.

(c) Oxidation of Side Chains. The vapour-phase oxidation of alkyl aromatic hydrocarbons results in the degradation of the side chains to give nuclear carboxylic acid groups. Thus both toluene and ethylbenzene give benzoic acid when passed over tin vanadate with air at 300° C. whereas *o*-xylene gives phthalic anhydride.

Partial oxidation products may also be produced, and Parks and Yula [58, 1941] describe the catalytic oxidation of toluene in the vapour phase to give benzaldehyde as well as maleic and benzoic acids. The catalyst was vanadium pentoxide on alfrax, and with temperatures of 380–460° C. optimum yields of partial oxidation products were obtained with a contact time of 0·5 sec.

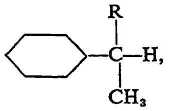
The liquid-phase oxidation of alkylaromatic hydrocarbons may be carried out by bubbling oxygen through the hydrocarbon at temperatures of about 120° C., usually in the presence of a catalyst such as the cobalt or manganese salts of napththenic or fatty acids. The site of oxidation is the carbon atom adjacent to the nucleus, and it is necessary for this carbon atom to carry a hydrogen atom in order to obtain oxidation under these conditions. Thus *tert.*-butyl benzene, which has no such hydrogen atom, is resistent to oxidation under conditions in which ethylbenzene and isopropylbenzene are readily oxidized.

The initial product of oxidation is a hydroperoxide which then decomposes to give ketonic or aldehydic products. These may be further oxidized to carboxylic acids.



The formation of small quantities of methylphenylcarbinol [Binapfl, 3, 1931] in the oxidation of ethylbenzene is considered to be due to side reactions and the alcohol is not thought to be the initial oxidation product [Senseman, 62, 1933].

Stephens and Roduta [72, 1935] examined a series of secondary alkyl aromatic hydrocarbons and found that the liquid-phase oxidation was not inhibited by the presence of water as was the case with normal alkyl aromatic hydrocarbons. It was further shown that with secondary alkyl aromatic hydrocarbons of the type



where R is greater than methyl, the ketone formed by oxidation was always acetophenone, thus indicating that the reaction involved the elimination of the larger alkyl group attached to the α-carbon atom.

The oxidation of alkylaromatic hydrocarbons containing two nuclear substituents may be illustrated by data available for the symenes. Senseman and Stubbs [63, 1932] obtained *p*-methylacetophenone, *p*-toluic acid, and terephthalic acid by the liquid-phase oxidation of *p*-cymene at 140–160° C., thus indicating that the initial oxygen attack is on the tertiary carbon atom of the isopropyl group. Palmer and Bibb [57, 1942], on the other hand, report the formation of cumic acid when a cymene is oxidized at a temperature below 140° C. in the presence of manganese and lead acetate. They also obtained tolylmethylketone and dimethyltolylcarbinol, and it is evident that both of the alkyl groups in the molecule of a cymene can form the site of initial oxygen attack.

Alkylation of the Aromatic Nucleus

Investigations into the Friedel–Crafts reaction [15, 1877] between aromatic compounds and alkyl halides in the presence of metal halide catalysts have been very numerous and the value and scope of the reaction have been considerably extended since its first discovery. The catalyst originally used was aluminium chloride, but many other compounds have since been found to catalyse the reaction. Alkyl halides, olefines, paraffins, naphthenes, alcohols, ethers, organic acids, acid chlorides and anhydrides, and organic and inorganic esters are among the classes of compounds which have been condensed with aromatic nuclei. Acids, acid chlorides, and acid anhydrides give rise to ketonic products, but the other compounds give alkylaromatic hydrocarbons.

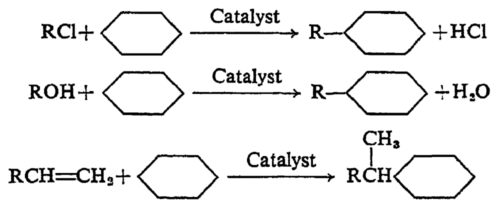
The presence of alkyl groups in the aromatic nucleus increases the reactivity of the hydrocarbon and there is therefore a tendency towards the formation of polyalkyl aromatics during the alkylation reaction. Suitable choice of reaction conditions can, however, either suppress or enhance the formation of poly derivatives. The reactivity of aromatic hydrocarbons also varies with different isomers. Thus Nakatsuchi [48, 1929] has found that 94% of *p*-xylene may be recovered unchanged from the alkylation of a mixture of xylene isomers with isobutylene. Similar observations on the relative rates of alkylation of the xylene isomers have been made by Nightingale and James [52, 1944].

The rate of reaction and the nature of the products obtained are also dependent upon the nature of the entering group. Generally, the most reactive compounds are those in which the functional group undergoing reaction is attached to a tertiary carbon atom, secondary compounds reacting less readily and primary compounds being the least reactive group. The reactivity of alkyl halides is further affected by the nature of the halogen atom in the group, the order of reactivity being $F > Cl > Br > I$. The number of substituents which can enter the nucleus depends on the structure of the entering group. Thus six *n*-propyl groups may be substituted in benzene but the number of isopropyl groups which can react is limited to four.

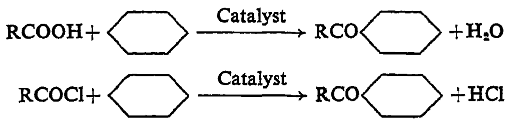
The catalysts used for the alkylation reaction may be divided into two classes, the metallic halides and the acidic catalysts. The former include the halides of metals such as aluminium, iron, tin, zinc, and boron, and the acidic catalysts include hydrogen fluoride, hydrogen chloride, sulphuric acid, phosphorus pentoxide, and phosphoric acid. The activity of these catalysts varies and their use in a given reaction depends upon the reactivity of the aromatic hydrocarbon and of the alkylating group. Thus a reactive halide such as benzyl chloride will react with benzene in the presence of a relatively weak catalyst such as zinc chloride, whereas a vigorous catalyst such as aluminium chloride is necessary for reaction with methyl chloride. The acidic catalysts are generally of greater use for the condensation of olefines and alcohols and the halide catalysts are used for reaction with alkyl halides. This may be illustrated by the results obtained for alkylation with a molecule such as allyl chloride, which has two different functional groups. In the presence of sulphuric acid condensation takes place principally at the double bond, but the chlorine atom is the site of reaction when ferric or zinc chlorides are used. A powerful catalyst such as aluminium chloride can cause reaction at both functional groups [Truffault, 76, 1936; Nenitzescu, 49, 1933]. The use of hydrogen chloride as a catalyst has recently been described by Simons and Hart [67, 1944]. It was found that good yields of alkyl aromatic hydrocarbons were obtained under pressures of about 200 lb. per sq. in. and at temperatures of 200° C.

Sachanen and Caesar [61, 1946] have described the use of a heterogeneous catalyst such as silica-alumina for the condensation of benzene with phthalic anhydride at 375° C. to form anthraquinone.

The reaction between alkyl halides, alcohols, and olefines may be written as indicated below. Various mechanisms have been suggested for the alkylation reaction, but reference should be made to original papers for detailed discussions of this subject.



Acids and acid chlorides react as follows:



Details of the use of hydrogen fluoride as a catalyst for the condensation of acids with aromatic hydrocarbons are given by Simons *et al.* [70, 1939].

The reaction between an ether and benzene to give an alkyl benzene is said to proceed via the intermediate formation of an olefine [O'Connor, 56, 1938], e.g.

$$(C_5H_{11})_2O \xrightarrow[BF_3]{} CH_3(CH_2)_2CH{:}CH_2+C_5H_{11}OH.$$

It might be expected that esters would give rise to ketonic products on alkylation, but these have been found only in small quantities when hydrogen fluoride is used as the catalyst [Simons, 69, 1939]. Bowden [6, 1938] showed that no ketones were formed when the catalyst was aluminium chloride. It was further shown by Bowden [loc. cit.] that those esters which reacted with aluminium chloride reacted either with difficulty or not at all in the presence of boron trifluoride.

When paraffins are reacted with aromatic hydrocarbons in the presence of aluminium chloride, the paraffin is broken at various points along the chain, and the fragments give rise to a mixture of alkylaromatic hydrocarbons and lower paraffins. This process is known as destructive alkylation, and according to Grosse and Ipatieff [21, 1935] it proceeds by scission of the paraffin to give a lower paraffin together with an olefine which immediately alkylates the aromatic hydrocarbon. The general equation for the reaction may be written:

$$C_{(m+n)}H_{(2(m+n)+2)}+ArH \xrightarrow[AlCl_3]{} C_nH_{(2n+2)}+ArC_mH_{(2m+1)}.$$

Thus 2,2,4-trimethylpentane and benzene give isobutane and mono-and di-*tert.*-butylbenzenes at 20° C. and atmospheric pressure [Grosse, 21, 1935; 23, 1938–9]. No reaction took place when boron trifluoride was used as the catalyst. In a further paper [24, 1938–9] Grosse *et al.* describe the reaction between benzene and paraffins ranging from pentane to *n*-hexadecane in the presence of aluminium chloride. In each case considerable breakdown of the paraffin molecule took place and paraffins, ranging from butanes to undecanes together with various alkyl aromatic hydrocarbons, were isolated.

Naphthenes such as cyclopropane, whose molecules are under strain, react with benzene to give, in this example, *n*-propyl benzene in the presence of aluminium chloride and hydrogen fluoride [Grosse, 22, 1937–8; Simons, 66, 1938]. Sulphuric acid, on the other hand, can give both normal and isopropylbenzene in this reaction [Ipatieff, 30, 1938; 31, 1940]. Cyclopentane did not react under these conditions.

Cyclic olefines, alcohols, and halides give the expected phenylnaphthenes on alkylation with benzene in the presence of aluminium chloride [Sidorova, 64, 1937; Corson, 11, 1937; Mayes, 42, 1929].

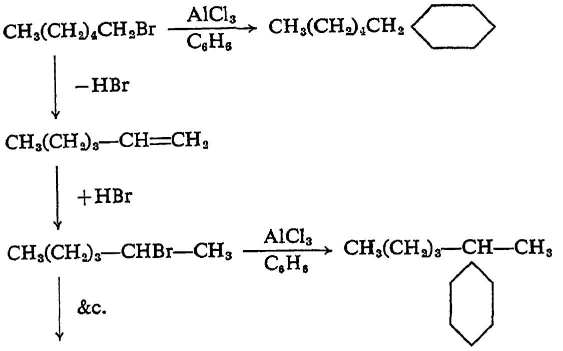
The Structure of the Products of Alkylation.

It has long been recognized that the product of an alkylation reaction is not always the simple compound which might be expected from the normal replacement of a nuclear hydrogen atom by the reacting alkyl group. The catalyst and the reaction conditions can cause isomerization of the entering alkyl group and also migration of the substituents within the nucleus.

Isomerization of the Alkyl Group.

The first case of isomerization to be noted was the formation of isopropylbenzene from both normal and isopropyl bromides and benzene in the presence of aluminium chloride. In their investigation of this isomerization Ipatieff *et al.* [31, 1940] found that at −6° C. the ratio of normal to isopropylbenzene was 3:2, whereas at 35° C. the ratio was 2:3. Bowden [6, 1938], on the other hand, found that alkylation with normal propyl esters gave *n*-propyl benzene. Other examples of isomerization which may be quoted are the formation of secondary from normal butyl compounds and the formation of tertiary from isobutyl compounds [McKenna, 43, 1937].

Gilman and Meals [19, 1943] have studied the reaction between alkyl halides of varying chain length and benzene in the presence of aluminium chloride. They found that the isomeric products formed contained hydrocarbons in which the phenyl group was located at various points along the alkyl chain. Thus *n*-hexyl bromide when condensed with benzene was found to give a mixture of 1-phenyl hexane, 2-phenyl hexane, and 3-phenyl hexane. There was, however, little evidence of any branching of the alkyl chain. The mechanism proposed for the reaction is one of elimination of hydrogen bromide from the alkyl halide molecule followed by addition in the reverse direction. This process would give rise to a series of alkyl halides with the halogen atom located at successive points along the carbon chain. These alkyl halides are considered to be the alkylating agents.



According to Ipatieff *et al.* [31, 1940], isomerization of the alkyl group occurs with olefines, alcohols, and naphthenes in the presence of sulphuric acid, but not in the presence of aluminium chloride. This is in agreement with the results obtained by Meyer and Bernhauer [44, 1929].

At higher reaction temperatures (80–95° C.) the entering alkyl group may be broken down in the presence of aluminium chloride. Norris and Sturgis [54, 1939] showed that benzene alkylated with *tert.*-butyl alcohol under these conditions gave toluene, ethylbenzene, and isopropylbenzene as products.

Orientation of the Alkyl Groups within the Nucleus.

The temperature of reaction and the catalyst used in the alkylation reaction can affect the position in the nucleus taken up by the entering group in relation to those already present. The normal rules of aromatic substitution indicate that the isomers to be expected on alkylation of an alkyl aromatic hydrocarbon are the ortho- and para-compounds. These are also the isomers to be expected when benzene is dialkylated. Aluminium chloride, however, is a powerful isomerizing catalyst [see Norris and Vaala, 55, 1939], and meta-compounds usually predominate in the reaction products when it is used as the condensing agent. Under mild conditions, however (0° C.), the alkylation of toluene with methyl chloride gives more ortho- than meta-xylene. At 106° C. the products were *m*- and *p*-xylene in the ratio of 50:1 [Norris, 53, 1939]. Similarly at 0° C. the trialkyl derivatives formed are the normal 1,2,4-compounds, whereas under the more vigorous conditions the 1,3,5-isomers are formed. The formation of these abnormal compounds in the alkylation reaction does not take place to any great extent when catalysts other than aluminium chloride are used, unless the formation of the normal compounds is prevented on stereochemical grounds. Thus sulphuric acid, hydrogen fluoride, boron trifluoride, and ferric chloride give the expected isomers.

Because of the possibility of the isomerizations and migrations discussed above, a great deal of work has been carried out to determine the structure of the products obtained in the alkylation reaction. In some of the earlier work the methods and data available for the identification of the products were not always satisfactory, and unless adequate proof is given, the structures assigned to the hydrocarbons should be regarded with caution.

Details of the experimental conditions and the yields obtained in many alkylation reactions are given in a review of the reaction by Price [59, 1946].

REFERENCES

1. Atanasin, I. A. *Bull. Chim. Soc., Române Chim.* **39**, 71–82 (1937–8).
2. Avanesov, D., and Vyatskin, I. *Trudy LKKh TI*, 1939, No. 7, 60–4, *Khim. Referat. Zhur.* **2**, No. 5, 43 (1939).
3. Binapfl, J., and Krey, W. U.S. Pat. 1,813,606 (7 July 1931).
4. Blanc, G. *Bull. Soc. Chim.* (4), **33**, 313 (1923).
5. Bone, W. A., and Newitt, D. M. U.S. Pat. 2,199,585 (7 May 1940).
6. Bowden, E. *J. Am. Chem. Soc.* **60**, 645 (1938).
7. Bullock, J. L., and Mitchell, E. T. *J. Am. Chem. Soc.* **63**, 3230 (1941); **65**, 2426 (1943).
8. Burgoyne, J. H. *Proc. Roy. Soc.* (*London*), A **174**, 394 (1940); A **175**, 539 (1940).
9. Burgoyne, J. H., and Newitt, D. M. *Proc. Roy. Soc.* (*London*), A **153**, 448 (1936).
10. Burgoyne, J. H., Tang, T. L., and Newitt, D. M. *Proc. Roy. Soc.* (*London*), A **174**, 379 (1940).
11. Corson, B. B., and Ipatieff, V. N. *J. Am. Chem. Soc.* **59**, 645 (1937).
12. Cutter, H. B., and Brown, H. C. *J. Chem. Edn.* **21**, 443 (1944).
13. Demann, W., Krebs, E., and Borchers, H. *Tech. Mitt. Krupp. Tech.* **6**, 59–63 (1938).
14. Doumani, T. F., and Kobe, K. A. *J. Org. Chem.* **7**, 1 (1942).
15. Friedel, C., and Crafts, J. M. *Compt. rend.* **84**, 1392, 1450 (1877).
16. Fuson, R. C., and McKeever, C. H. *Organic Reactions*, vol. **1**, p. 63. Published by John Wiley (1942).
17. Gattermann, L. A., and Berchelmann, W. *Ber.* **31**, 1149, 1765 (1898).
18. Gattermann, L. A., and Koch, J. A. *Ber.* **30**, 1622 (1897).
19. Gilman, H., and Meals, R. N. *J. Org. Chem.* **8**, 126 (1943).
20. Grassi-Cristaldi, G., and Maselli, C. *Gazzetta*, **28**, ii. 477 (1898).
21. Grosse, A. V., and Ipatieff, V. N. *J. Am. Chem. Soc.* **57**, 2415 (1935).
22. ——— *J. Org. Chem.* **2**, 447 (1937–8).
23. Grosse, A. V., Mavity, J. M., and Ipatieff, V. N. *J. Org. Chem.* **3**, 448 (1938–9).
24. ——— *J. Org. Chem.* **3**, 137 (1938–9).
25. Harman, R. A. U.S. Pat. 2,382,148 (14 Aug. 1945).
26. Hey, D. H. *J. Chem. Soc.* **138**, 72 (1935).
27. Hinkel, L. E., Ayling, E. E., and Morgan, W. H. *J. Chem. Soc.* **135**, 2793 (1932).
28. Holloway, J. H., and Krase, N. W. *Ind. Eng. Chem.* **25**, 497 (1933).
29. Ingold, C. K., Lapworth, A., Rothstein, E., and Ward, D. *J. Chem. Soc.* **134**, 1959 (1931).
30. Ipatieff, V. N., Pines, H., and Corson, B. B. *J. Am. Chem. Soc.* **60**, 577 (1938).
31. Ipatieff, V. N., Pines, H., and Schmerling, L. J. *J. Org. Chem.* **5**, 253 (1940).
32. Kazanskii, B. A., and Glushnev, N. F. *J. Gen. Chem.* (*U.S.S.R.*), **8**, 642 (1938).
33. ——— *Bull. Acad. Sci. U.R.S.S. Classe Sci. Math. Nat. Ser. Chim.* 1061 (1938).
34. Kazanskii, H. A., and Smirnova, N. V. *Bull. Acad. Sci. U.R.S.S. Classe Sci. Math. Nat. Ser. Chim.* 547 (1937).
35. Kharasch, M. S., and Brown, H. C. *J. Am. Chem. Soc.* **61**, 2142 (1939).
36. Kharasch, M. S., McBay, H. C., and Urry, W. H. *J. Org. Chem.* **10**, 401 (1945).
37. Kharasch, M. S., and Read, A. T. *J. Am. Chem. Soc.* **61**, 3089 (1939).
38. Kobe, K. A., and Doumani, T. F. U.S. Pat. 2,353,312 (11 July 1944).
39. ——— *Ind. Eng. Chem.* **33**, 170 (1941).
40. Kobe, K. A., and Lueth, P. F. *Ind. Eng. Chem.* **34**, 309 (1942).
41. Lock, G. *Ber.*, **74b**, 1568 (1941).
42. Mayes, H. A., and Turner, E. E. *J. Chem. Soc.* **132**, 500 (1929).
43. McKenna, J. F., and Sowa, F. J. *J. Am. Chem. Soc.* **59**, 1204 (1937).
44. Meyer, H., and Bernhauer, K. *Monatsh.* **53** and **54**, 721–52 (1929).
45. Milas, N. A. *J. Am. Chem. Soc.* **59**, 2342 (1937).
46. Morton, A. A., Little, E. L., and Strong, W. O. *J. Am. Chem. Soc.* **65**, 1339 (1943).
47. Moyer, W. W. U.S. Pat. 2,328,920 (7 Sept. 1943).
48. Nakatsuchi, A. *J. Soc. Chem. Ind. Japan*, **32**, Suppl. binding, 335 (1929).
49. Nenitzescu, C. D., and Isacescu, D. A. *Ber.* **66b**, 1200 (1933).
50. Niedzielski, E. L., and Nord, F. F. *J. Am. Chem. Soc.* **63**, 1462 (1941).
51. ——— *J. Org. Chem.* **8**, 147 (1943).
52. Nightingale, D., and James, J. R. *J. Am. Chem. Soc.* **66**, 154 (1944).
53. Norris, J. F., and Rubinstein, D. *J. Am. Chem. Soc.* **61**, 1163 (1939).
54. Norris, J. F., and Sturgis, B. M. *J. Am. Chem. Soc.* **61**, 1413 (1939).
55. Norris, J. F., and Vaala, G. T. *J. Am. Chem. Soc.* **61**, 2131 (1939).
56. O'Connor, M. J., and Sowa, F. J. *J. Am. Chem. Soc.* **60**, 125 (1938).
57. Palmer, R. C., and Bibb, C. H. U.S. Pat. 2,302,462 (17 Nov. 1942).
58. Parks, W. G., and Yula, R. W. *Ind. Eng. Chem.* **33**, 891 (1941).
59. Price, C. C. *Organic Reactions*, vol. **3**, p. 1. Published by John Wiley (1946).
60. Rueggeberg, W. H., Frantz, R. K., and Ginsburg, A. *Ind. Eng. Chem.* **38**, 624 (1946).
61. Sachanen, A. N., and Caesar, P. D. *Ind. Eng. Chem.* **38**, 43 (1946).
62. Senseman, C. E., and Stubbs, J. J. *Ind. Eng. Chem.* **25**, 1286 (1933).
63. ——— *Ind. Eng. Chem.* **24**, 1184 (1932).
64. Sidorova, N. V., and Tsukervanik, I. P. *J. Gen. Chem.* (*U.S.S.R.*), **7**, 641 (1937).
65. Simons, J. H., *et al.* Report of work by: *Chemical Industries*, **59**, 1011 (1946).
66. Simons, J. H., Archer, S., and Adams, E. *J. Am. Chem. Soc.* **60**, 2955 (1938).
67. Simons, J. H., and Hart, H. *J. Am. Chem. Soc.* **66**, 1309 (1944).
68. Simons, J. H., Passino, H. J., and Archer, S. *J. Am. Chem. Soc.* **63**, 608 (1941).
69. Simons, J. H., Randall, D. I., and Archer, S. *J. Am. Chem. Soc.* **61**, 1821 (1939).
70. ——— *J. Am. Chem. Soc.* **61**, 1795 (1939).
71. Smith, L. I. *Organic Reactions*, vol. **1**, p. 370. Published by John Wiley (1942).
72. Stephens, H. N., and Roduta, F. L. *J. Am. Chem. Soc.* **57**, 2380 (1935).
73. Thomas, R. J., Anzilotti, W. F., and Hennion, G. F. *Ind. Eng. Chem.* **32**, 408 (1940).
74. Titov, A. I. *J. Gen. Chem.* (*U.S.S.R.*), **10**, 1878 (1940).
75. Titov, A. I., and Baeryshnikova, A. N. *J. Gen. Chem.* (*U.S.S.R.*), **6**, 1801 (1936).
76. Truffault, R. *Compt. rend.* **202**, 1286 (1936).
77. Vavon, G., Bolle, J., and Calin, J. *Bull. Soc. Chim.* **6**, 1025 (1939).
78. Westheimer, F. H., Carmack, M., *et al.* *J. Am. Chem. Soc.* **69**, 773, 785 (1947).
79. Whitmore, F. C., and Ginsburg, A. *Ind. Eng. Chem.* **38**, 474 (1946).
80. Wilson, R. E., and Fuller, E. W. *Ind. Eng. Chem.* **14**, 406 (1922).

THE CHEMISTRY OF OLEFINE AND DIOLEFINE HYDROCARBONS

By F. A. FIDLER

Anglo-Iranian Oil Co. Ltd.

SINCE the previous article was written in Volume II by Farmer and Thorpe [26, 1938], the importance of olefines and diolefines for the production of chemicals has increased enormously. The main source of raw materials for organic chemicals in the past was coal tar, but the stage has already been reached where, in the U.S.A., the production of chemicals from petroleum is already exceeding that from the older coal-tar industry.

The availability of olefines and diolefines on the present enormous scale is due to the development of special cracking methods for producing them. In gasoline cracking processes in addition to the gasoline fraction, ethylene, propene, and the butenes were also produced on a scale considerably larger than had ever been available before. Two distinct attacks were made on the problem of utilizing these waste materials, the first being to convert them into useful fuels by polymerization and the second to convert them into chemicals. This article attempts to summarize the chemistry of the reactions of the olefine hydrocarbons with particular reference to their commercial utilization.

Condensation of Olefines with Organic Acids, Acid Chlorides, and Acid Anhydrides

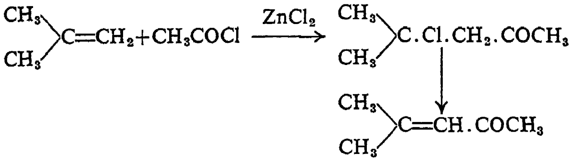
In the presence of certain catalysts, olefines can be made to condense with organic acids, acid chlorides, or acid anhydrides. The primary products obtained from these condensations are esters, chloroketones, or unsaturated ketones respectively. Each of these reactions will be discussed in turn.

The production of esters from olefines and acids using catalysts such as sulphuric acid or zinc chloride has been known for many years, but it is in only relatively recent years that a process has been developed suitable for large-scale operation. This was the result of the gradually increasing demand for esters as solvents, plasticizers, lubricants, &c. Edlund, Evans, and Taylor [16, 1935; 17, 1936; 23, 1938] were successful in developing a satisfactory process for the manufacture of butyl and amyl acetates using acetic acid, refinery cuts from cracking operations, and sulphuric acid as catalyst.

Cracked C_4 fractions contain isobutene and the normal butenes, and if these are condensed with acetic acid they yield *tert.*- and *sec.*-butyl acetates respectively. Similarly the pentene-pentane cut gives *sec.*- and *tert.*-amyl acetates with acetic acid. Since the most desirable esters are the secondary ones, the preferred procedure is to remove the more reactive tertiary olefines prior to esterification. For instance, treatment of the C_4 fraction with 55 to 60% sulphuric acid in the cold will remove the isobutene almost completely and leave the normal butenes unaffected.

For the production of the ester, the olefine-containing cut is contacted with acetic acid and 95% sulphuric acid at 60° C. for a sufficient length of time to attain equilibrium. The product separates into two layers, the upper one containing unreacted hydrocarbon and ester and the lower one sulphuric acid and unreacted acetic acid. The ester is recovered from the former while the latter, after the addition of a small amount of fresh sulphuric acid, is recirculated with more olefine and acetic acid.

The primary product from the reaction between acid chlorides and an olefine should be a chloroketone, but these compounds are relatively unstable and easily lose hydrogen chloride giving unsaturated ketones. Kondakow [57, 1894] showed that in the presence of zinc chloride, acetyl chloride condensed with isobutene to give methylchloroisobutyl ketone which on heating gave mesityl oxide.



$$(CH_3)_2C{=}CH_2+CH_3COCl \xrightarrow{ZnCl_2} (CH_3)_2C.Cl.CH_2.COCH_3 \longrightarrow (CH_3)_2C{=}CH.COCH_3$$

Mesityl oxide.

The aluminium halides have also been found to be satisfactory catalysts for this condensation. Krapivin [58, 1908], using aluminium chloride and bromide in carbon disulphide or hexane, condensed acetyl chloride or bromide with olefines ranging from ethylene to octene. The products of the reactions were unsaturated ketones ranging from butenone to a decenone.

A considerable amount of research has been carried out to determine the mechanism of the reaction and the constitution of the products formed, summaries of which are given in Carleton Ellis, *The Chemistry of Petroleum Derivatives* [22, 1934, 1937]. The general conclusion is that the primary products from the condensation of acid chlorides and olefines in the presence of aluminium chloride are chloroketones but these are not always isolated owing to their readiness to lose hydrogen chloride. Other catalysts which have been found suitable are titanium and stannic chloride.

Byrnes and Doumani [7, 1943] have shown that in the presence of zinc chloride or sulphuric acid, acid anhydrides condense with branched-chain olefines to give unsaturated ketones according to the equation

$$C_nH_{2n}+(RCO)_2O \longrightarrow C_nH_{2n-1}COR+RCOOH.$$

The olefines employed by these workers were diisobutene and a polymer gasoline obtained from the copolymerization of propene and butenes over a phosphoric acid catalyst, since these are readily available in large quantity. The principal product from the former was 4,6,6-trimethyl-3-heptene-2-one which is formed from 2,2,4-trimethylpentene-1, the preponderant isomer in diisobutene. Two narrow boiling cuts were taken from the polymer gasoline, the yields of ketones being 53% from the 90° to 100° C. cut and 57% from the 100° to 110° C. boiling fraction.

Of the condensing agents tried, zinc chloride was found to be most satisfactory. Sulphuric acid was quite effective, but suffered from the disadvantage that it also caused a certain amount of olefine polymerization. Aluminium chloride was also a poor catalyst for the reaction, giving a low yield of ketone due to the considerable polymerization which occurred.

Condensation of Olefines with Alcohols

In the presence of concentrated sulphuric acid, Evans and Edlund [24, 1936] showed that tertiary olefines will condense with alcohols to form *tert.*-alkyl ethers. Organic sulphonic acids and aluminium chloride are also catalysts for the reaction, but sulphuric acid was found to be the most satisfactory. The reaction is reversible and reaches an equilibrium which varies with the olefine and alcohol used. Isobutene reacts very rapidly with methanol and the equilibrium lies well on the ether side.

$$CH_3OH + i\text{—}C_4H_8 \rightleftharpoons CH_3.O.C_4H_9(tert.).$$

With diisobutene, however, practically no reaction whatever takes place. Primary alcohols are more suitable than secondary for this condensation, while the tertiary alcohols react only slightly if at all.

The Condensation of Paraffins with Olefines

The alkylation of paraffins with olefines has developed in the last decade into one of the most important of refinery processes, and is described in detail in another article. A brief survey only will be given here.

Frey and Hepp showed that paraffins reacted with olefines in the absence of catalysts by heating to 500° C. at a pressure of 4,500 lb. per sq. in. Under these conditions, ethylene and isobutane gave a liquid product containing a considerable proportion of 2,2-dimethylbutane.

However, the production of alkylate commercially as a blending agent for 100-octane aviation spirit has been carried out catalytically, the catalysts used being sulphuric acid, hydrogen fluoride, and aluminium chloride. Sulphuric acid and hydrogen fluoride are only effective as catalysts for the reaction of olefines and isoparaffins, no reaction occurring with the normal paraffins. Little information has been published on the hydrogen fluoride alkylation process, but it has been shown that isobutane and isopentane condense with propene and the C_4 and C_5 olefines to give higher boiling isoparaffins.

$$iso\text{-}C_4H_{10} + C_3H_6 \longrightarrow C_7H_{16}.$$

In commercial operation, the temperature of the reaction is maintained between 24° and 46° C., the heat of reaction being removed by external cooling, and the pressure sufficient to maintain the reactants in the liquid phase.

The literature on sulphuric acid alkylation is much more extensive since this was developed to a commercial scale before the war. If an olefine such as isobutene is added to a well-stirred mixture of isobutane and concentrated sulphuric acid, condensation occurs between the hydrocarbons to produce an alkylate consisting mainly of isooctanes.

$$iso\text{-}C_4H_8 + iso\text{-}C_4H_{10} \longrightarrow iso\text{-}C_8H_{18}.$$

The reaction is carried out at a temperature between 0° and 10° C. using a large excess of isobutane. On the commercial scale, the olefines which have been reacted with isobutane are propene, the butenes, and the pentenes obtained from thermal and catalytic cracking units.

As already stated, aluminium chloride activated with hydrogen chloride differs from the two acid catalysts in that it will bring about the alkylation of normal paraffins with olefines. This is probably due to the fact that the catalyst is also effective for isomerizing normal paraffins to isoparaffins and in this case isomerization precedes alkylation. The principal product from the alkylation of isobutane with ethylene in the presence of aluminium chloride has been shown to be 2,3-dimethylbutane.

The Alkylation of Aromatic Hydrocarbons with Olefines

Aromatic hydrocarbons are alkylated with olefines in the presence of catalysts such as aluminium chloride, sulphuric acid, phosphoric acid, and hydrogen fluoride to produce alkylaromatics. The chemistry of this reaction is fully dealt with under 'The Chemistry of Aromatic Hydrocarbons'.

The production of aromatic hydrocarbons from benzene and olefine containing feedstocks has been used commercially for a variety of purposes. Ethylbenzene is an essential hydrocarbon for synthetic rubber production since on dehydrogenation it produces styrene. Although present in coal tar and petroleum, the separation from the accompanying xylenes is difficult and, owing to the high purity demanded, it was made synthetically. Considerable quantities were produced by the ethylation of benzene using an aluminium chloride catalyst.

An extremely useful aromatic blending component of 100-octane aviation gasoline during the war was isopropylbenzene or cumene. For the manufacture of this hydrocarbon, benzene was passed with a propene fraction from reforming units over a phosphoric acid catalyst.

In Germany during the war alkylaromatics were sulphonated to produce synthetic detergents of the aryl alkyl sulphonate type. The necessary aromatics with long alkyl side chains were manufactured by the reaction of olefines, such as the polymers of propene, with benzene or xylene in the presence of hydrogen fluoride.

Alkylation of Phenols with Olefines

The alkylation of phenols with olefines is in many ways similar to the alkylation of aromatics with unsaturated hydrocarbons. Catalysts which have been used for this reaction are sulphuric acid [25, 1936; 73, 1934; 38, 1934], aluminium chloride [80, 1937], hydrogen fluoride [8, 1939], and phosphoric acid [40, 1936].

In the presence of sulphuric acid, tertiary olefines react to produce the *p-tert.*-alkyl phenols. For instance, Natelson [73, 1934] showed that when phenol was stirred with isobutene, amylene, or diisobutene in the presence of concentrated sulphuric acid at a temperature below 10° C., the products obtained were *tert.*-butyl, *tert.*-amyl, and *tert.*-octylphenol. Ipatieff, Pines, and Friedman [39, 1938] repeated the reaction with diisobutene and obtained in addition to *p-tert.*-octyl phenol, a compound which appeared to be 2,4-di-*tert.*-octyl phenol. If a mixture of phenol and diisobutene was agitated with a large excess of sulphuric acid and the temperature allowed to rise to 85° C., the product contained a quantity of *p-tert.*-butylphenol. With phosphoric acid at 150° C. the yield of octylphenol was very low, although some *p-tert.*-butylphenol was isolated. The alkylation of isobutene with phosphoric acid at 100° C. gave *p-tert.*-butylphenol and 2,4-di-*tert.*-butylphenol in 40 and 30 % yields respectively.

Smith and Rodden [80, 1937] alkylated phenol with diisobutene in the presence of aluminium chloride. The reaction was carried out on a steam bath and yielded a mixture of *p-tert.*-butylphenol and *p-tert.*-octylphenol. The ratio of these two in the product could be thrown almost completely in either direction by varying the reaction conditions, less vigorous conditions favouring the latter.

Calcott, Tinker, and Weinmayr [8, 1939] showed that hydrogen fluoride was a suitable catalyst for the alkylation of phenols with olefines and from *m*-cresol and propene obtained diisopropyl-*m*-cresol.

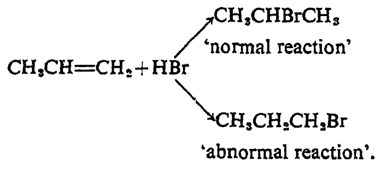
The octylphenol formed from diisobutene and phenol has been used for germicidal, fungicidal, and bactericidal purposes. It is also a most important intermediate in the preparation of synthetic detergents of the Igepal type [9, 1946]. The octylphenol is condensed with ethylene oxide to give an alkyl phenol polyglycol ether. This itself can be used as a detergent or emulsifying agent or is converted to the sodium sulphonate.

Reactions of Halogen Acids with Olefines

Hydrogen halides add to the double bond of olefines to give alkyl halides. To explain the products obtained, Markovnikoff [62, 1870] formulated a rule which stated that the addition of a halogen acid to an unsymmetrical olefine occurs so that the halogen adds to the carbon atom with the fewer hydrogen atoms. For instance, the addition of hydrogen chloride to propene gives isopropyl and not *n*-propyl chloride.

$$CH_3CH{=}CH_2+HCl \longrightarrow CH_3CHCl{-}CH_3.$$

This rule has been found to apply satisfactorily when hydrogen chloride, fluoride, or iodide is used as the acid. However, many anomalies were reported when hydrogen bromide was employed. As a result, a considerable amount of confusion existed, and it was mainly due to the work of Kharasch, Mayo, and co-workers that the problem was cleared up. They showed that in many cases if the pure halogen acid and pure olefine are reacted in the dark in the absence of oxygen and catalysts, then the product formed obeys Markovnikoff's rule and 'normal reaction' occurs. However, if small quantities of oxygen or peroxides are introduced into the reaction mixture, an 'abnormal reaction' takes place and the halogen acid adds to the double bond in the reverse way. This is illustrated by the reaction with propene:



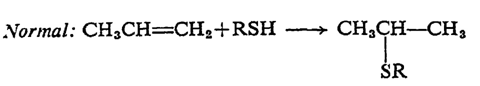
$$CH_3CH{=}CH_2+HBr \begin{cases} \nearrow CH_3CHBrCH_3 & \text{'normal reaction'} \\ \searrow CH_3CH_2CH_2Br & \text{'abnormal reaction'.} \end{cases}$$

This has become known as the 'peroxide effect' and in many cases it has been possible to isolate both of the possible products in a pure condition according to whether oxygen and peroxides have been excluded from the reaction or not. Mechanisms have been proposed to explain this abnormal addition, reviews of which are given by Mayo and Walling [63, 1940] and Smith [79, 1939].

Vaughan and Rust [93, 1946] have shown that abnormal addition also occurs if a mixture of the olefine, hydrogen bromide, and a carbonyl compound such as an aldehyde or ketone is irradiated with light of wave-length capable of dissociating the catalyst.

Reaction of Olefines with Hydrogen Sulphide, Mercaptans, and Thiophenol

In the reaction with an olefine, hydrogen sulphide and mercaptans behave in a manner analogous to that of halogen acids in that they can form both 'normal' and 'abnormal' addition products. For example, with propene and a mercaptan the two reactions which can occur are:



$$\textit{Normal: } CH_3CH{=}CH_2+RSH \longrightarrow CH_3\underset{\displaystyle SR}{\underset{|}{C}}H{-}CH_3$$

$$\textit{Abnormal: } CH_3CH{=}CH_2+RSH \longrightarrow CH_3CH_2CH_2SR.$$

Jones and Reid [45, 1938] showed that, in the presence of sulphur, hydrogen sulphide adds to olefines by the normal reaction and the products are those expected from Markovnikoff's rule. Without sulphur, little if any reaction occurs. However, it has been shown that, under certain conditions, hydrogen sulphide can be made to add on to olefines by the abnormal reaction. This can be effected by irradiating the olefine–hydrogen sulphide mixture at room temperature with light of wave-length below 2,900 Å or with light of wave-length above 3,000 Å in the presence of certain carbonyl compounds such as ketones, aldehydes, and acid halides [94, 1946]. These catalysts are dissociated by the light and act as chain initiators for the abnormal addition reaction of hydrogen sulphide to the olefine.

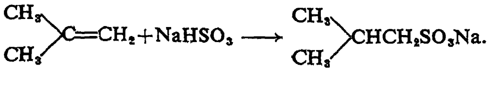
In the case of the addition of mercaptans to olefines, the most usual reaction is the one giving abnormal products and this is catalysed by oxygen, peroxides, or light of wave-length less than 3,000 Å. As with hydrogen sulphide, Vaughan and Rust have shown that the photo-chemical process in the presence of carbonyl compounds also proceeds with mercaptans to give 'abnormal' addition. If these catalytic reagents are excluded from the reaction, the addition is retarded and may be completely stopped. The only 'normal' addition of mercaptans to olefines which has been found is one in which sulphur [45, 1938] has been used as catalyst.

Ipatieff, Pines, and Friedman [42, 1938] showed that in the absence of acid catalysts, thiophenol reacts with propene, butene-1, pentene-1, and isopropylethylene to give products by the abnormal addition. However, in the presence of sulphuric acid diluted with water or acetic acid, the normal product was obtained. Ninety per cent. phosphoric acid had no influence on the course of the reaction and abnormally orientated products were obtained. Ipatieff and Friedman [43, 1939] extended the work to mercaptans and thioacetic acid. The reactions were carried out in a stainless steel bomb without the addition of a definite catalyst, although oxygen and traces of peroxides were not excluded. In all cases, good yields of thioethers and thioesters were obtained, with structures contrary to those predicted by Markovnikoff's rule.

Recently Cunneen [13, 1947] has reacted cyclohexene and methylcyclohexene with thioglycollic acid, thiophenol, and isopentanethiol and has confirmed that in each of these cases, under peroxide conditions, the addition to an asymmetrically substituted double bond proceeds via the abnormal reaction.

Reaction of Olefines with Sodium Bisulphite

Kharasch, May, and Mayo [48, 1938] investigated the reaction between ethylene, propene, and isobutene and bisulphites at room temperature. It was found that, in the absence of oxygen, no reaction occurred. However, the admission of air brought about addition, the extent depending on the amount of air admitted. The products obtained were all primary sulphonates and therefore corresponded to abnormal addition to the double bond.



$$(CH_3)_2C{=}CH_2+NaHSO_3 \longrightarrow (CH_3)_2CHCH_2SO_3Na.$$

Reaction of Thiocyanogen with Olefines

Thiocyanogen reacts with olefines to produce dithiocyanates. Dermer and Dysinger [15, 1939] showed that if thiocyanogen, produced from sodium thiocyanate and copper sulphate, was mixed with certain olefines in glacial acetic acid, dithiocyanates were obtained. These had satisfactory melting-points and might be used for identifying the olefines.

	m.p. (°*C.*)
Ethylene dithiocyanate	90·0– 90·5
Styrene dithiocyanate	102·5–103.0
Cyclohexene dithiocyanate	58·0– 58·5
3-Methylcyclohexene-1-dithiocyanate	69·5– 70·0

Propene, the butenes, and the amylenes yielded only liquid thiocyanates which showed no tendency to crystallize. Naylor [74, 1945] also obtained a liquid 1,2-dithiocyano-1-methylcyclohexane from 1-methylcyclohexene and thiocyanogen in chloroform. This dithiocyanate solidified on cooling to 0° C.

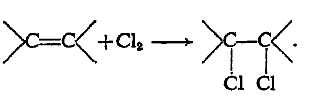
A recent review on the reactions of thiocyanogen [101, 1946] includes a description of the three methods available for carrying out thiocyanation. Thiocyanogen can be liberated in a free state in organic solvents by the action of oxidizing agents on thiocyanic acid or metal thiocyanates. The most convenient method of employing this technique is by the addition of bromine to a thiocyanate. The second method involves the electrolysis of concentrated solutions of alkali thiocyanates, while the third method is the action of cupric sulphate on sodium thiocyanate. The cupric thiocyanate formed releases thiocyanogen and becomes converted to the cuprous salt.

$$2Cu(SCN)_2 \longrightarrow 2CuSCN+(SCN)_2.$$

The action of thiocyanogen on olefines has been applied as a method for the estimation of the unsaturated content of hydrocarbon mixtures by Krassilchick and co-workers [37, 1929; 59, 1936]. The reagent is prepared by the action of bromine on lead thiocyanate in glacial acetic acid.

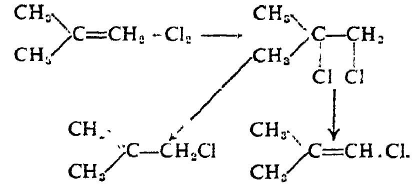
Addition of Halogens to Olefines

Probably the best-known reaction of all unsaturated compounds is the addition of halogens.



Their high reactivity to halogens distinguishes them from paraffins and naphthenes. Furthermore, this reaction is so distinctive that it is widely employed in the estimation of unsaturated hydrocarbons in gasolines. The usual halogen used for this purpose is bromine, as in the Francis method, since this element reacts more quickly than either chlorine or iodine.

The usual product obtained by the addition of a halogen is the dihalide; for example ethylene and chlorine give ethylene dichloride or dichlorethane. However, when more than one isomer is possible, as with the butenes and pentenes, different products can be formed. Butene-1 and butene-2 with chlorine give the dihalides but isobutene yields a mixture of chlorobutenes. This is due to the instability of dichlorisobutane which readily loses hydrogen chloride.

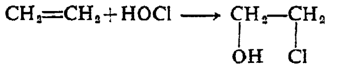


In many cases, particularly if the olefine possesses reactive hydrogen atoms, substitution as well as addition can also take place to produce polyhalides.

Vaughan and Rust [95, 1940] have studied the high-temperature chlorination of olefines and have demonstrated that both the addition and substitution reactions occur by radical chain mechanisms. The inclusion of small concentrations of oxygen catalyses the substitution reaction, although in larger concentrations it acts as an inhibitor.

Reaction of Olefines with Hypochlorous Acid

Olefines react with hypochlorous acid to give chlorhydrins, the simplest member being ethylene chlorhydrin.



$$CH_2{=}CH_2+HOCl \longrightarrow \underset{OH}{CH_2}{-}\underset{Cl}{CH_2}$$

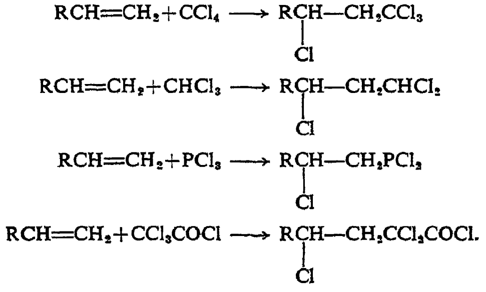
Ethylene chlorhydrin.

Numerous methods have been suggested for the preparation of this compound. One of these is by the action of chlorine water and ethylene, the procedure used being to pass the olefine and chlorine simultaneously into water. A second process is the direct addition of hypochlorous acid, this being formed by the action of gaseous carbon dioxide on bleaching powder.

Hydrolysis of the chlorhydrin with a weak alkali such as sodium bicarbonate produces ethylene glycol.

The Addition of Polyhalogenated Compounds and Olefines

Kharasch, Jensen, and Urry have investigated the reaction of octene-1 with polyhalogenated compounds such as chloroform [49, 1945], carbon tetrachloride [49, 1945], chlorinated acetic acids [50, 1945], phosphorus trichloride [51, 1945], carbon tetrabromide [52, 1946], and bromoform [52, 1946]. The catalysts used for all of these reactions were diacyl peroxides, viz. diacetyl or dibenzoyl peroxide. It was shown that in every case one halogen atom added to the β-carbon atom and the residue of the molecule added to the end of the chain. Typical reactions which occurred were:



$$RCH{=}CH_2+CCl_4 \longrightarrow \underset{Cl}{RCH}{-}CH_2CCl_3$$

$$RCH{=}CH_2+CHCl_3 \longrightarrow \underset{Cl}{RCH}{-}CH_2CHCl_2$$

$$RCH{=}CH_2+PCl_3 \longrightarrow \underset{Cl}{RCH}{-}CH_2PCl_2$$

$$RCH{=}CH_2+CCl_3COCl \longrightarrow \underset{Cl}{RCH}{-}CH_2CCl_2COCl.$$

It will be noticed that with trichloracetyl chloride it is the halogen attached to the α-carbon atom which becomes detached and adds to the olefine. In the case of carbon tetrabromide, it was found that the addition was also catalysed by visible light.

The Action of Sulphuric Acid on Olefines

The reactions of sulphuric acid and olefines can be many and varied and are dependent on the structure of the olefine, the strength of the acid, the ratio of acid to olefine, the temperature of reaction, and the time of contact between the acid and hydrocarbon.

The reactivity of olefines towards the acid increases with molecular weight of the olefines from ethylene through propene and the butenes to the hexenes. When ethylene is contacted with concentrated sulphuric acid, the reactions which take place are:

$$C_2H_4+H_2SO_4 \longrightarrow C_2H_5HSO_4,$$
$$C_2H_5HSO_4+C_2H_4 \longrightarrow (C_2H_5)_2SO_4.$$

The initial product is ethyl sulphuric acid which with more ethylene becomes converted into diethyl sulphate. The same reactions occur with propene and sulphuric acid, but in this case the acid concentration should be reduced or the temperature lowered below room temperature, otherwise considerable polymerization occurs. The absorption of ethylene and propylene in sulphuric acid to give alkyl sulphuric acids is used in the production of ethyl and isopropyl alcohols, the latter being formed on hydrolysis of the alkyl hydrogen sulphates.

The butenes and pentenes are more reactive with sulphuric acid than ethylene or propene, and if it is required to produce the alcohols, by absorption of the olefines in acid followed by hydrolysis, the strength of the acid must be carefully controlled otherwise considerable polymer formation may take place. The reactivity varies with the structure of the olefine, tertiary olefines being more readily polymerized than the straight-chain hydrocarbons. It is therefore possible to separate the olefine types by treating a mixture with definite strengths of sulphuric acid. In the case of the C_4 olefines, only isobutene is absorbed in the cold by 65% sulphuric acid, it being necessary to used acid of 75 to 85% for the sulphation of butene-1 and butene-2. Hydrolysis of these sulphuric acid solutions yields *tert.*- and *sec.*-butyl alcohols respectively. If the temperature of the solution of isobutene in sulphuric acid is raised, polymerization of the olefine occurs, producing isobutene polymers. This is the procedure employed for the manufacture of diisobutene and triisobutene from a cracked C_4 cut which contains all the C_4 olefines and paraffins.

Similar reactions to those discussed above for the butenes also take place with the pentenes. The isomers containing a tertiary grouping, namely, trimethylethylene and methylethylethylene, are absorbed with 60 to 70% acid and are polymerized if the acid concentration is higher than this. Pentene-1 and pentene-2, however, resemble the butenes and require acid of 75 to 85% concentration before sulphation occurs at ordinary temperature.

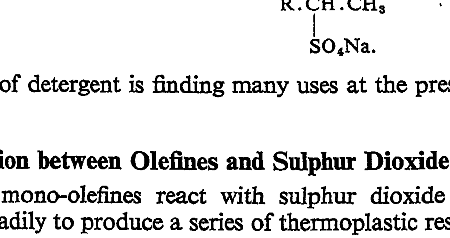
Approximately 20 years ago, Ormandy and Craven [76, 1927] investigated the method for the estimation of unsaturateds by absorption in sulphuric acid. They found, unexpectedly, that when an olefine was shaken with concentrated sulphuric acid and allowed to stand, an oil separated out which was not a polymer of the olefine used. Instead it contained large proportions of saturated hydrocarbons, which they concluded were largely open-chain paraffins. This was the first time that this observation had been made. Ipatieff and Pines [41, 1936] and Nametkin [72, 1936] repeated this work and also found that saturated hydrocarbons were produced by the action of concentrated sulphuric acid on olefines. Ormandy and Craven [76, 1927] also pointed out that if the acid layer was diluted with water, a highly unsaturated material was thrown out of solution. The term 'hydropolymerization' has been applied to this type of reaction by Nametkin [72, 1936].

Ipatieff and Pines [41, 1936] investigated the action of sulphuric acid on a large number of olefines at varying temperatures, different concentrations of acid, and various ratios of acid to olefine. They concluded that with large amounts of concentrated sulphuric acid at 0° C., olefines yielded a mixture of paraffins, olefines, and cyclo-olefines. The fractions boiling below 250° C. contained entirely saturated hydrocarbons, the olefines and cyclo-olefines appearing in the fractions above this temperature. If the ratio of acid to olefine was considerably reduced, then the products formed had a much higher boiling-range and olefines were present in the material boiling below 250° C. When the sulphuric acid layer was diluted with water, an oil separated which appeared to be a cyclo-olefine of the general formula C_2H_{2n}—4. The formation of paraffinic or cyclic hydrocarbons was only observed if concentrated acid was employed, since acid below 90% did not bring about hydropolymerization but merely straight polymerization to open-chain olefines.

It therefore appears that with strong acid, polymerization occurs together with hydrogenation-dehydrogenation, producing saturated hydrocarbons on the one hand and highly unsaturated cyclic compounds on the other. Studies on the nature of the dehydropolymer in the acid layer have been made by Hartig, Hughes, and Veatch [33, 1946], using ultra-violet absorption spectroscopy. These workers found that the spectrum was consistent with the view that it contains a conjugated double-bond system with a naphthenic ring such as would be found in a substituted cyclopentadiene.

The sulphation of straight-chain olefines having between 12 and 20 carbon atoms in the chain has also been used for the manufacture of synthetic detergents.

The most useful olefines for this purpose are the *a*-olefines, the double bond being at the end of the chain. These can be obtained by the cracking of wax at high temperatures with a very short time of contact. The olefines are sulphated with acid usually of 90 to 96% concentration, and the alkyl sulphuric acids neutralized to the sodium salts.



$$R.CH{=}CH_2+H_2SO_4 \longrightarrow \underset{\displaystyle SO_4H}{\underset{|}{RCH}}\text{—}CH_3 \;\downarrow\; R.\underset{\displaystyle SO_4Na}{\underset{|}{CH}}.CH_3$$

This type of detergent is finding many uses at the present time.

Reaction between Olefines and Sulphur Dioxide

Simple mono-olefines react with sulphur dioxide extremely readily to produce a series of thermoplastic resins. A considerable amount of research and development work in this reaction has been carried out by Frey and his co-workers.

The reaction between mono-olefines and sulphur dioxide involves equimolecular proportions of the reactants and takes place at ordinary temperatures. Frey and Snow [81, 1938, 1943] showed that, in the absence of light and catalysts, no reaction occurred over prolonged periods of time, and that one of these was an essential requisite for the reaction to take place. As a result of their researches, the following conclusions were drawn:

(*a*) Light of wave-length less than 3,800 Å or a catalyst is necessary to effect the polymerization reaction between sulphur dioxide and olefines.

(*b*) The catalyst should be soluble in the reaction mixture or react with it to produce a soluble catalyst.

(*c*) The most effective catalysts for bringing about the reaction are oxidizing agents or oxygen-containing compounds.

Typical compounds which were found to exert strong catalytic activity were organic peroxides such as benzoyl peroxide and the nitrates of silver, lithium, and ammonium.

An interesting feature of these sulphur dioxide–olefine polymerizations is that each particular olefine has a 'ceiling temperature' above which it will not react with sulphur dioxide. A most striking case is that of isobutene. At room temperature no reaction takes place between this olefine and sulphur dioxide, even in the presence of a catalyst, but if the reaction mixture is cooled to 4° C. polymerization proceeds smoothly and satisfactorily. On warming to room temperature, however, reaction again ceases. Furthermore, isobutene is a potent inhibitor in the *n*-butene-sulphur dioxide condensation, 10% of the former olefine slowing down the room temperature reaction of the latter to one-tenth of its normal rate.

The Reaction of Olefines with Dioxane Sulphotrioxide

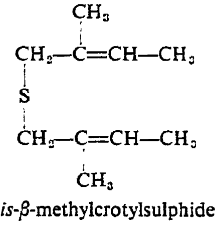
Suter [86, 1938; 87, 88, 1941] has used dioxane sulphotrioxide and disulphotrioxide as sulphonating agents for olefines. The reagent is prepared by adding sulphur trioxide to dioxane in an inert solvent such as carbon tetrachloride or ethylene dichloride. On passage of propene into the reagent suspended in ethylene dichloride, the solid disappeared, giving a clear colourless solution. The product was not isolated, but was hydrolysed with alkali to give a hydroxypropane sulphonate. If isobutene is treated with the reagent the product formed is methyl-2-propene-1-sulphonic acid or 2-methylpropene-1,3-disulphonic acid according as to whether an excess of the reagent is employed or not.

Reaction of Olefines with Sulphur

The reaction between ethylene and sulphur in xylene solution has been investigated by Westlake, Mayberry, Whitlock, West, and Haddad [98, 1946], who found that at temperatures between 125° and 140° C. and initial pressures of 140 to 160 lb. per sq. in., two types of product were formed. One was soluble and the other insoluble in xylene, and the latter increased at the expense of the former as the reaction time was increased. In pilot plant experiments it was shown that the xylene solution could be recycled without any increase in concentration of the soluble products, although considerable quantities of the xylene insoluble materials were formed. They concluded that the insoluble material was a polymer of the soluble product. Tentative structures for these were put forward.

If the temperature of the reaction reached 180° C. all the sulphur was converted into xylene-soluble ethylene polysulphides, there being no insoluble materials formed and no free sulphur left.

Armstrong, Little, and Doak [1, 1944] reacted a number of olefines such as butene-2, 2-methyl-butene-1, &c., with sulphur in the presence of various vulcanizing ingredients in order to clarify the mechanism of rubber vulcanization. They were able to isolate from these reactions, which were carried out at 120° to 140° C. with stirring, a mixture of mono- and di-sulphides with certain amounts of polysulphides and polymer. Determinations of the structures of the monosulphides showed that the principal products of the reaction of sulphur with simple olefines in the presence of vulcanizing agents are those in which the olefine is bridged by sulphur at the *a*-methylene carbon atoms. For instance, it has been demonstrated by ozonolysis that the product from 2-methyl-butene-2 contained *bis*-*β*-methylcrotylsulphide.

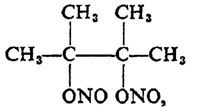


$$\begin{array}{l} CH_2-\overset{CH_3}{C}=CH-CH_3 \\ \ \ | \\ \ \ S \\ \ \ | \\ CH_2-\underset{CH_3}{C}=CH-CH_3 \end{array}$$

bis-*β*-methylcrotylsulphide.

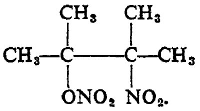
Action of Nitrogen Tetroxide on Olefines

The products formed by the reaction between olefines and nitrogen tetroxide are rather confusing and until recently the evidence has not been conclusive as to the constitution of the compounds formed [77, 1945]. For instance, Schmidt [78, 1903] believed the compound formed between tetramethylethylene and nitrogen tetroxide using ether as solvent was a dinitrite:



$$CH_3-\underset{ONO}{\overset{CH_3}{C}}-\underset{ONO,}{\overset{CH_3}{C}}-CH_3$$

but Demjanov [14, 1904] concluded that the main product was a nitronitrate:



$$CH_3-\underset{ONO_2}{\overset{CH_3}{C}}-\underset{NO_2.}{\overset{CH_3}{C}}-CH_3$$

Michael and Carlson [65, 1940] carried out a careful investigation of this reaction and their conclusions were:

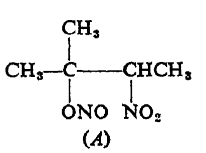
(*a*) In ether solution approximately 20% of 2,3-dinitro-2,3-dimethylbutane was formed.

(*b*) Without a solvent or in petroleum ether, the yield of dinitro compound was very low.

(*c*) The nitronitrate of Demjanov was formed in all cases, the yield depending on the experimental conditions.

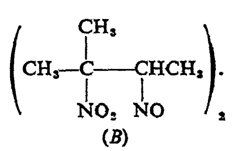
(*d*) Schmidt's dinitrite was not formed.

The same observers also studied the reaction between nitrogen tetroxide and trimethylethylene [66, 1937]. The main reaction products were shown to be a nitronitrite (*A*) and a dimeric nitronitroso compound (*B*).



$$CH_3-\underset{ONO}{\overset{CH_3}{C}}-\underset{NO_2}{CHCH_3}$$

(*A*)



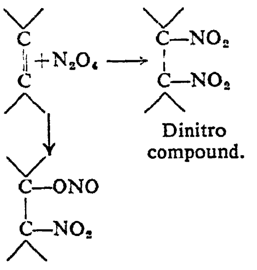
$$\left(CH_3-\underset{NO_2}{\overset{CH_3}{C}}-\underset{NO}{CHCH_3}\right)_2.$$

(*B*)

Intensive work on the action of nitrogen tetroxide on simple olefines has recently been reported by Levy, Scaife, and Smith [61, 1946]. They state that the reasons for the previous confusion were:

(*a*) the nitrogen tetroxide used was impure;
(*b*) oxidative side reactions also occur;
(*c*) some of the primary products undergo further reaction;
(*d*) some of the primary products are very unstable.

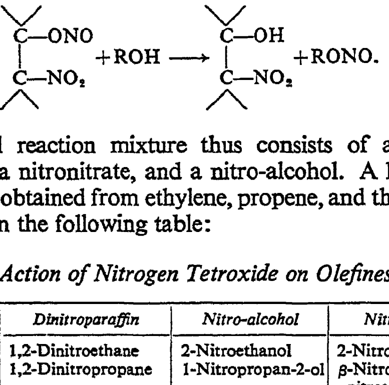
Levy *et al.* reacted pure nitrogen tetroxide with olefines with or without a solvent, maintaining the temperature at or below room temperature by means of external cooling. Under these conditions only two primary reactions occur, the products being the dinitroparaffin and the nitronitrite.



Dinitro compound.

Nitronitrite.

The nitronitrite is unstable and is readily oxidized to the nitronitrate. The method of working up the reaction product developed by these workers was to remove the excess dinitrogen tetroxide and solvent and then convert the nitronitrite into a nitro-alcohol immediately by treatment with water or alcohol.



The final reaction mixture thus consists of a dinitroparaffin, a nitronitrate, and a nitro-alcohol. A list of the products obtained from ethylene, propene, and the butenes is given in the following table:

The Action of Nitrogen Tetroxide on Olefines

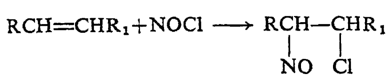
Olefine	*Dinitroparaffin*	*Nitro-alcohol*	*Nitronitrate*
Ethylene	1,2-Dinitroethane	2-Nitroethanol	2-Nitroethylnitrate
Propene	1,2-Dinitropropane	1-Nitropropan-2-ol	β-Nitroisopropyl-nitrate
Isobutene	1,2-Dinitroisobutane	Nitro-*tert.*-butanol	Nitro-*tert.*-butyl-nitrate
Butene-1	1,2-Dinitro-*n*-butane	1-Nitrobutan-2-ol	..
Butene-2	2,3-Dinitro-*n*-butane	2-Nitrobutan-3-ol	..

It will be seen that for unsymmetrical olefines, the nitronitrite reaction occurs so that the nitro group becomes attached to the carbon atom with the greater number of hydrogen atoms, and the nitrite group to the carbon atom with the fewer hydrogen atoms. In general, both forms of addition, i.e. the formation of the dinitro and nitronitrite compounds, occur to a similar extent.

Bond [5, 1946] has shown that the reaction of nitrogen tetroxide with olefines can be used for the determination of the unsaturation of a gasoline. Aromatics, naphthenes, and paraffins are unattacked by nitrogen tetroxide under the conditions of test whilst the olefines form oily products which can readily be separated from the unchanged hydrocarbons.

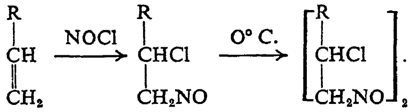
The Addition of Nitrosyl Chloride to Olefines

Nitrosyl chloride adds to olefines to yield compounds having a nitroso group and a chlorine atom attached to the carbon atoms forming the double bond:



$$RCH{=}CHR_1 + NOCl \longrightarrow \underset{NO}{\underset{|}{RCH}}-\underset{Cl}{\underset{|}{CHR_1}}.$$

Some of these nitroso compounds are nicely crystalline solids and can be utilized for purposes of identification. A certain amount of confusion exists in the literature regarding the melting-points of some of the compounds, but this is probably due to the use of different isomers. For instance, from amylene, Sudborough [85, 1891] obtained an addition compound with a melting-point of 152° C., but Tilden and Forster [92, 1894] gave the melting-point of the product from amylene and nitrosyl chloride as 74° to 75° C. Spengler and Moldner [84, 1944] studied this reaction using long-chain normal olefines with the double bond in the α-position. Nitrosyl chloride was added to the olefine in ether at −40° C. and the temperature allowed to rise slowly for a period of 20 hours. Under these conditions a dimeric nitrosochloride separated out. The reaction is given by:



$$\begin{matrix}R\\|\\CH\\\|\\CH_2\end{matrix} \xrightarrow{NOCl} \begin{matrix}R\\|\\CHCl\\|\\CH_2NO\end{matrix} \xrightarrow{0^\circ C.} \left[\begin{matrix}R\\|\\CHCl\\|\\CH_2NO\end{matrix}\right]_2.$$

These dimeric compounds were extremely stable and the three prepared had the following melting-points:

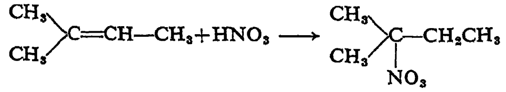
Olefine	*Melting-point of dimeric nitrosochloride*
	°C.
Nonene-1	81·8
Tridecene-1	92·0
Pentadecene-1 . . .	94·5

It was demonstrated that, in the case of propene, nitrosyl chloride added so that the nitroso group became attached to the end carbon atom and the chlorine atom to the middle carbon atom. By analogy, it was therefore assumed that the same method of addition occurred with the long-chain olefines.

The reaction between olefines and nitrosyl chloride has been used for the preparation of surface active agents [2, 1942]. Cracked petroleum cuts containing between 10 and 30 carbon atoms in the molecule were converted to the nitrosochlorides and these subsequently treated with sodium sulphite. By this process the chlorine atom is replaced by a sulphonate group, which gives the compounds valuable water-solubilizing properties.

Addition of Nitric Acid to Olefines

Michael and Carlson [67, 1935] showed that although 98·6% nitric acid did not add to ethylene, butene-1, or cyclohexene, addition did take place with trimethylethylene and isobutene. In the case of the former olefines, oxidation products only were obtained. However, with the tertiary olefines, *tert.*-alkyl esters were produced in good yields if the reaction was carried out in an inert solvent such as carbon tetrachloride at −20° C. *tert.*-Amyl nitrate was formed from 2-methylbutene-2 according to the equation:



tert.-Amyl nitrate.

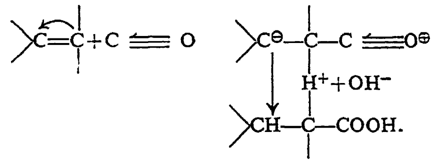
Condensation Reactions of Carbon Monoxide and Olefines

Under certain conditions, olefines react with carbon monoxide and steam to produce carboxylic acids:

$$R.CH{=}CH_2+CO+H_2O \longrightarrow R.CH_2CH_2COOH.$$

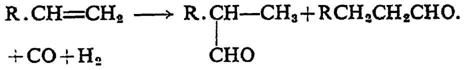
Many catalysts have been used to bring about this reaction and are described in a number of duPont patents taken out between 1933 and 1936. Hardy [31, 1936] showed that ethylene, propene, and butene-2 reacted in the presence of carbon monoxide and steam and a phosphoric acid catalyst to produce propionic, isobutyric, pivalic, methylethyl acetic, and higher acids. The conditions employed were 150 atm. and 290° to 300° C. for ethylene and 200 atm. and 200° C. for propene and butene.

Hardy suggested that the mechanism for this reaction was activation of the olefine molecule, which then added carbon monoxide and the elements of water:



A reaction involving carbon monoxide and olefines which is proving of considerable interest is the so-called OXO synthesis. This was discovered by Roelen in Germany, who found that aldehydes were present in the reaction products from ethylene and carbon monoxide-hydrogen mixtures at low pressures in the presence of cobalt catalysts. The importance of the reaction was soon appreciated and a considerable amount of work both on the chemical and plant development side resulted.

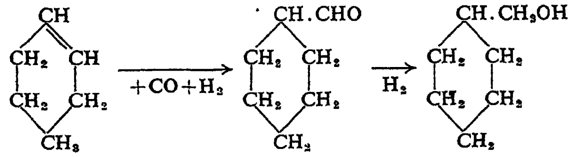
The reaction which occurs is given by the equation:



$$\begin{array}{l} R.CH{=}CH_2 \longrightarrow R.\underset{\displaystyle CHO}{\underset{|}{C}H}{-}CH_3+RCH_2CH_2CHO. \\ +CO+H_2 \end{array}$$

Thus ethylene gives propionaldehyde, whilst other olefines usually give more than one aldehyde according to the carbon atom to which the formyl group is attached. In the German process the aldehydes were hydrogenated immediately to the corresponding alcohols.

The product becomes more complicated with the higher olefines since under the conditions of the reaction, isomerization of the olefine takes place. Thus even from a pure olefine, there are generally more than two isomeric aldehydes formed. Cyclic olefines react in the same manner as the aliphatic hydrocarbons, the fully hydrogenated product from cyclohexene being cyclohexyl carbinol.



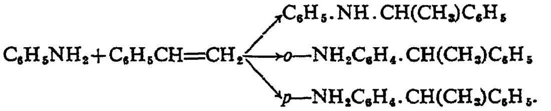
The products formed depend also on the structure of the olefine, since the formyl group does not attach itself to a quaternary carbon atom and with some molecules, addition is sterically hindered. In addition to the expected aldehydes, a certain amount of high-boiling aldehyde polymers are also formed during the reaction.

The most satisfactory conditions for carrying out the OXO synthesis are between 100° and 150° C. and at a pressure of 120 to 160 atm. The olefine is reacted with water gas which has a carbon monoxide hydrogen ratio of approximately 1 to 1·25. In the German plants the catalyst most frequently used was a normal Fischer-Tropsch catalyst comprising cobalt, thoria, and magnesia supported on kieselguhr.

Reactions of Olefines with Ammonia and Amines

Although it has been stated [97, 1925] that the reaction of ammonia and ethylene over a reduced ammonium molybdate catalyst produces ethylamine, the main effort with this reaction has been concentrated on the production of nitriles from ammonia and olefines [90, 1946]. Teter and collaborators obtained nitriles from olefines using iron, cobalt, or nickel catalysts at temperatures from 400° to 725° F. and at pressures ranging from several atmospheres to 3,000 lb. per sq. in. It was shown that in this reaction a mixture of nitriles was obtained even with pure olefines. Propene, for example, reacted to give aceto-, proprio-, isobutyro-, *n*-butyro-, and *n*-valero-nitriles in varying proportions. The same mixture was obtained if a C_2/C_3 cut from cracker gases was employed, while dodecene gave 4·4% acetonitrile, 89·0% lauronitrile and monolaurylamine, and 6·6% dilaurylamine.

The addition of aniline and *p*-toluidine to olefines has been investigated by Hickinbottom [35, 1932, 1934, 1935], who showed that when styrene was treated with aniline in the presence of its hydrobromide or hydrochloride at 220° to 260° C., two types of product were obtained according as to whether substitution occurred in the ring or on the amino group.



$$C_6H_5NH_2+C_6H_5CH{=}CH_2 \begin{cases} \nearrow C_6H_5.NH.CH(CH_3)C_6H_5 \\ \longrightarrow o{-}NH_2C_6H_4.CH(CH_3)C_6H_5 \\ \searrow p{-}NH_2C_6H_4.CH(CH_3)C_6H_5. \end{cases}$$

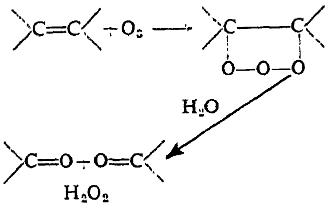
Also when trimethylethylene was heated in a sealed tube with aniline hydrobromide at 245° to 250° C. the product formed was a mixture of *p*-amino-*tert*.-amylbenzene and N-*tert*.-amylaniline. The proportion of the two products depended on the experimental conditions; a considerable excess of aniline and small amounts of the hydrobromide favoured the formation of the amylaniline. The structure of the olefine also had some effect; octene gave *sec*.-octylaniline as the principal product, but tetramethylethylene under similar conditions gave mainly the *p*-aminotetramethylethylbenzene with only a small amount of the alkylaniline.

Oxidation of Olefines

The oxidation of unsaturated hydrocarbons has been studied with a wide variety of reagents. The direct oxidation of ethylene with oxygen formed a subject of study for many years. The early workers such as Bone, Wheeler, and collaborators found that the reaction of oxygen and ethylene in the absence of catalysts produced formaldehyde [see 22*a*, 1934]. However, the main commercial use of ethylene oxidation has been the production of ethylene oxide. This is carried out by the passage of ethylene with air over a silver catalyst activated with copper or gold.

The double bond in unsaturated hydrocarbons forms a point of attack for many oxidizing agents such as ozone, potassium permanganate, chromic acid, &c. The reaction of olefines with ozone was first observed by Harries [32, 1905], who showed that addition occurred to form ozonides.

These, on warming with water, decomposed into aldehydes or ketones and hydrogen peroxide.



This has since been used as the standard method for determining the structures of compounds containing double bonds. An example of this was the determination of the proportion of the isomers in diisobutene. McCubbin and Adkins [64, 1930] found that the ratio of the methylneopentyl ketone to acetone and trimethylacetaldehyde was approximately 4 to 1 and from this they concluded that the ratio of 2,4,4-trimethylpentene-1 to 2,4,4-trimethylpentene-2 in diisobutene had the same value. This was later confirmed by Whitmore and Church [99, 1932], who separated the individual olefines by fractionation and ozonized them separately.

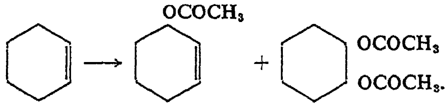
Dilute potassium permanganate in the cold oxidizes the double bond in an olefine producing a glycol. Oxidation with strong aqueous permanganate, however, produces acids and may, if the pH is not controlled with magnesium sulphate or carbon dioxide, bring about complete degradation.

In recent years a number of more selective oxidizing agents have been employed, some of which are described below.

Lead tetra-acetate in acetic acid has been used by Criegee [11, 1930] for the oxidation of olefinic hydrocarbons. This reagent reacts in the following manner:

$$Pb(OCOCH_3)_4 \longrightarrow Pb(OCOCH_3)_2 + 2(—OCOCH_3).$$

The acetate groups then attack methylene groups next to the double bond or add on to the double bond directly, e.g.

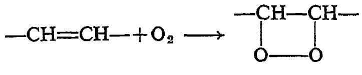


Hydrogen peroxide has been used as a most effective oxidizing agent for olefines by Milas and his collaborators. Milas and Sussman [68, 1936] used hydrogen peroxide in anhydrous tertiary butanol in the presence of osmium tetroxide, and with olefines such as isobutene and trimethylethylene obtained the corresponding glycols. Other catalysts for this hydroxylation reaction with hydrogen peroxide in butanol are vanadium pentoxide and chromium trioxide [69, 1937]. Using the former, the yield of trimethylene glycol from its olefine was 36%. Milas and Sussman [70, 1937] have shown that the glycols formed by this method invariably have the *cis* configuration while those formed via the hypochlorite route or by the intermediate formation of an epoxide have as a rule the *trans* configuration.

Another reagent which produces *cis* glycols from olefines is a cold aqueous solution of sodium chlorate with osmium tetroxide or vanadium pentoxide as catalyst [36, 1913; 6, 1929].

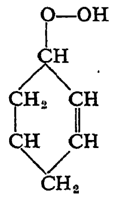
Use has recently been made of performic and peracetic acids for the hydroxylation of olefinic hydrocarbons [89, 1946]. Swern and his co-workers have shown that performic acid, which is formed by dissolving hydrogen peroxide in formic acid, when reacted with a number of 1-olefines produced excellent yields of 1,2-diols. The formic acid in this reagent forms the dual purpose of solvent and oxygen carrier since performic acid is the intermediate oxidizing agent. They oxidized straight-chain olefines having an even number of carbon atoms from C_8 to C_{18} and found that it was necessary to employ only 1·025 to 1·05 moles of peroxide per mole of olefine. The yields of pure glycols varied between 40 and 70% theoretical. With peracetic acid, the olefines formed epoxides, but the yields were much lower than those obtained with performic acid.

A considerable amount of attention has recently been given to the mechanism of the autoxidation of olefines [96, 1945]. These reactions, which are autocatalytic, are activated by light and catalysts such as peracids and peroxides and inhibited by such compounds as quinol. The accepted theory was that a moloxide was formed by the addition of an oxygen molecule to the double bond.



Moloxide.

However, Farmer [28, 1942] has shown that the reaction which usually occurs at moderate temperatures is the formation of a hydroperoxide on a carbon atom adjacent to the double bond. This confirmed the work of Criegee [12, 1939], who had stated that the compound formed by the action of molecular oxygen on cyclohexene was cyclohexene hydroperoxide.



Cyclohexene hydroperoxide.

Farmer and Sundralingham [28, 1942] prepared the hydroperoxides of 1-methyl and 1,2-dimethylcyclohexene and showed that these compounds decompose spontaneously or by the action of heat. The point of attack of the molecular oxygen is always on the carbon atom in the α-position to the double bond and is due to the lability of the hydrogen atom of the α-methylene group.

An excellent review of the present theories regarding the mechanism of auto-oxidation is given by Waters [96, 1945].

Polymerization of Olefines

The polymerization of olefine feedstocks, usually obtained from thermal or catalytic reforming operations, to produce high-octane gasolines has employed chemists in the petroleum industry for some considerable time. Subsequent hydrogenation of such polymers as diisobutene and codimer provided valuable components for aviation fuels in the recent war. Excellent reviews of the use of numerous catalysts such as sulphuric and phosphoric acids have already been given [22*b*, 1937], and this aspect of polymerization was dealt with fully in the previous article on 'The Chemistry of Hydrocarbons' [26, 1938]. It is therefore intended to deal exclusively with one or two aspects of polymerization which have reached commercial importance in the last few years.

The first is the production of polythene [29, 1946]. This refers to a series of solid polymers produced by the high-pressure polymerization of ethylene. The discovery of this reaction was due to a number of workers of the I.C.I. in 1933. The polymerization is carried out at a pressure of 1,200 atm. at 200° C. in the presence of a small but accurately measured percentage of oxygen. The reaction is highly exothermic. For the production of these polymers the ethylene must be rigidly purified. Polythene has chemical properties comparable with those of paraffin wax, but its superior mechanical and electrical properties give it insulating properties of much wider application than wax.

Another field which assumed first-rate importance during the war, particularly in Germany, is the production of synthetic lubricants by olefine polymerization. The synthesis of lubricating oils having high viscosity indices by the action of aluminium chloride on olefines has been known for some considerable time, but the cost of such processes compared unfavourably with the cost of production of lubricants directly from petroleum. However, owing to the scarcity of naturally occurring mineral oils in Germany, synthetic processes were developed on a large scale there for supplementing the natural supplies. A review of such processes is given by Spaght [82, 1946], who interviewed a number of German personnel and saw plants for the production of synthetic lubricants from olefines.

Two feedstocks were used, these being either ethylene or olefine produced from the cracking of Fischer-Tropsch material or paraffin wax. The polymerizing catalyst for both feedstocks was aluminium chloride. In the case of ethylene, it was necessary first to prepare the liquid catalyst by passing ethylene into a slurry formed of aluminium chloride and recycle polymer. During this stage a considerable evolution of heat occurred and the temperature rose rapidly to between 180° and 220° C. The mixture was then cooled to 110° to 140° C. to complete the catalyst preparation. The ethylene was fed into this mixture at as high a rate as possible while maintaining the temperature at a desired figure.

It was found that if a highly viscous oil was required, the peak temperature during catalyst preparation was limited to 180° C. and the temperature of polymerization was maintained at 110° C. However, if an oil of lower viscosity was required, the maximum temperature during catalyst make was 220° C., which produced a less active catalyst, while the polymerization temperature was kept at 140° C.

The reaction normally employed approximately 6 hours, after which time the excess ethylene was removed, the temperature reduced, and the oil layer separated from the aluminium chloride sludge. Removal of catalyst from the oil and distillation gave the desired polymer. The use of ethylene for synthetic lubricant production was mainly developed by the I.G. workers under the direction of Dr. H. Zorn.

Ruhrchemie favoured the higher olefines as starting-material for the aluminium chloride polymerization. The olefines were obtained by the cracking of a cut from Fischer-Tropsch oil or by the cracking of paraffin wax. In both cases the bulk of the olefines were α-olefines. The polymerization was carried out for 15 to 20 hours at a temperature of between 60 and 80° C.

The polymers both from the ethylene and liquid olefines had very similar chemical and lubricating properties, with viscosity indices of 110 to 120 and pour-points around −15° F. They were used almost entirely in aircraft engines.

Isomerization of Olefines

Unlike the isomerization of paraffins, the isomerization of olefines includes several different types of reactions, some of which are:

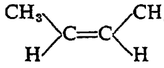
1. Movement of the double bond.
2. Interconversion of *cis* and *trans* isomers.
3. Branching of the chain.

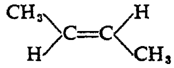
A considerable amount of work has been carried out on the isomerization of the lower olefines such as the butenes and pentenes [see 18, 1942] both in the presence and absence of catalysts. Little has been reported, however, on the isomerization of pure olefines in the spirit range.

Hurd and Goldsby [38, 1934] showed that butene-2 isomerizes exclusively to butene-1 at temperatures of 500° to 700° C., but Ipatieff, Pines, and Schaad [44*a*, 1934] were able to carry out this isomerization at much lower temperatures in the presence of catalysts. With orthophosphoric acid, the following conversions were obtained:

Temperature, °C.		26	78	100	135
% by volume	Butene-1	96	88	66	40
	Butene-2	4	12	34	60

In the case of butene-1, only one form exists, but butene-2 can exist in both *cis* and *trans* forms.


cis-Butene-2


trans-Butene-2.

Both these forms have been prepared and characterized, and it has been concluded from a study of their properties that the lower boiling isomer has the *trans* configuration. The kinetics of the *cis*-*trans* conversion of butene-2 have been investigated by Kistiakowsky and Smith [56, 1936], who showed that at 390° C. the ratio of *cis* to *trans* was 47·2 to 52·8.

A number of catalysts have been found which effect the isomerization of *n*-butenes to isobutene. Egloff and collaborators [19, 1939] showed that in the temperature range 385° to 600° C. using a silica-alumina catalyst, the *n*-butenes underwent extensive isomerization to isobutene accompanied by polymerization and cracking. The *n*-pentenes showed reactions similar to the butenes, yielding 50% of isopentenes at 400° C.

From the point of view of utilization of the olefines as fuels, the isomers having the highest octane value are those with the double bond in the middle of the chain or possessing a highly branched carbon skeleton. The straight-chain members with the double bond at the end of the chain have the lowest octane ratings. With a view to converting the 1-olefines into more useful isomers, Hay, Montgomery, and Coull [34, 1945] investigated the isomerization of hexene-1 over several catalysts in the temperature range 285° to 500° C. Their results indicated that the catalysts must be acidic or have absorbed hydrogen ions to bring about skeletal isomerization and, furthermore, the reaction proceeded stepwise through methylpentenes to dimethylbutenes.

$$\text{hexene-1} \longrightarrow \text{methylpentenes} \longrightarrow \text{dimethylbutenes}.$$

The most effective catalysts used by these authors were phosphoric acid on kieselguhr, acid-treated activated alumina, superfiltrol, and acid-treated sodium permutite. They found that although the reaction rates increased with temperature, the extent of isomerization decreased with increasing temperature. At the space velocity used, namely, 0·6 hour^{-1}, the optimum isomerization temperature was 375° C.

Berg, Summer, and Montgomery [3, 1946] attempted to improve the octane ratings of cracked distillates by isomerization of the olefines present. The most suitable catalyst they used was alumina impregnated with hydrogen chloride, by the employment of which the octane number of a thermally cracked distillate containing approximately 40% olefines was increased by four numbers.

Co-ordination Compounds between Olefines and Metallic Salts

The property of olefines to form co-ordination compounds with various metallic salts has been known for some considerable time. The reaction is a general one, and a wide variety of metals have been shown to possess the ability to form complex compounds with unsaturated hydrocarbons. Some of the more important ones are platinum, palladium, copper, silver, mercury, and aluminium. The compounds from platinum, cuprous, silver, and mercuric salts are readily formed by the passage of the gaseous olefine into an aqueous solution of the metallic salt. The most satisfactory method of preparing the platinum complexes is by treating a solution of platinic bromide in an anhydrous solvent such as benzene or glacial acetic acid with the olefine [47, 1941]. These complexes, $(PtBr_2.Olefine)_2$, are crystalline compounds. Kharasch, Seyler, and Mayo [53, 1938] showed that a useful method for preparing the palladium compounds was by reacting the palladous chloride–benzonitrile complex with the olefine. The reaction which occurs is:

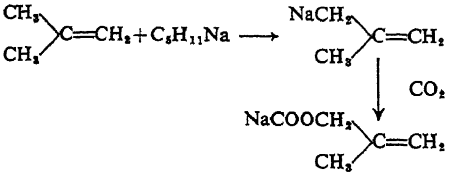
$$2(C_6H_5CN)_2PdCl_2+2\text{ olefine}\longrightarrow(PdCl_2Olefine)_2+4C_6H_5CN.$$

Compounds with ethylene and isobutene were prepared using this technique. Molecular weight determinations on platinum and palladium-olefine compounds suggest that they have a doubled molecular formula [54, 1936].

Many theories have been put forward in an attempt to explain the structures of the various co-ordination compounds. A critical review of these is given by Kelly [47, 1941], who reaches the conclusion that no one theory has yet been put forward which explains all cases of metallic salt–olefine complex formation.

The Metallation of Olefines

Morton and co-workers [71, 1945] have recently shown that olefines can be converted by amylsodium to alkenyl sodium reagents. The latter, on carbonation, give unsaturated acids which are normally not available by other means. For example, isobutene is readily attacked by amylsodium to give a product which on carbonation yields β-methylvinyl acetic acid.



$$(CH_3)_2C{=}CH_2+C_5H_{11}Na\longrightarrow (NaCH_2)(CH_3)C{=}CH_2\xrightarrow{CO_2}(NaCOOCH_2)(CH_3)C{=}CH_2$$

In addition, a certain amount of β-methylene-glutaric acid is also formed due to dimetalation.

Pentene-1 gives two sodium compounds, 1-pentenyl-3-sodium, $CH_2{=}CHCH(Na)C_2H_5$ and 1-pentenyl-1-sodium, $NaCH{=}CHC_3H_7$ in the ratio of 4 to 1 respectively.

Chemistry of the Diolefines

There are three types of diolefines depending on the situation of the double bonds in the molecule. These are:

1. With the double bonds adjacent, the simplest member being allene.

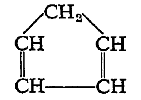
$$CH_2{=}C{=}CH_2$$

Allene

2. With the double bonds in alternate positions, examples of this being butadiene and cyclopentadiene.

$$CH_2{=}CH{-}CH{=}CH_2$$

Butadiene



Cyclopentadiene

This type of compound is termed a conjugated diolefine.

3. With the double bonds separated by more than one single bond, such as is found in diallyl.

$$CH_2{=}CH{-}CH_2{-}CH_2{-}CH{=}CH_2$$

Diallyl

This is a non-conjugated diolefine.

Of these three types, the most important from a petroleum viewpoint are the conjugated diolefines, since these are the ones found in cracked gasolines. Also, they are most valuable for synthetic purposes since they condense readily with a wide variety of reagents. The chemistry of the allenes and non-conjugated diolefines has not advanced materially since the previous article was written in Volume II of *Science of Petroleum*, and consequently this review will be concerned exclusively with the conjugated members.

Production of Butadiene.

In the last few years diolefine chemistry has been almost completely monopolized by one member of this class, namely, butadiene. In the United States and in Germany during the war more effort was placed into the production of butadiene than into that of any other single hydrocarbon. As is well known, this is one of the basic materials for the synthetic rubbers and as such was made on an enormous scale in the United States. The subject of synthetic rubbers is beyond the scope of this article, but since much of the butadiene was prepared from petroleum sources, a brief review of the methods of production will be given.

Butadiene is a constituent of the C_4 fraction obtained by the pyrolysis of many hydrocarbons. From the point of view of fuels, diolefines are only a nuisance since they polymerize readily and are largely responsible for gum formation in gasolines. Consequently, thermal or catalytic reforming for the production of motor fuels is carried out at temperatures which give minimum quantities of diolefines.

There are two main types of compounds which have been used for the production of butadiene, the first being hydrocarbons and the second oxygen derivatives of hydrocarbons. Exhaustive surveys of both these have been given by Egloff and Hulla [20, 1944, 1945]. The processes considered here are those which have been employed for large-scale manufacture. Figures for the production of butadiene by the various reactions in the United States have been given in articles by Elder [21, 1942] and Frolich and Morrell [30, 1943].

A method which, although worked out in Russia, was developed principally in Germany, involved the condensation of acetaldehyde to aldol using dilute alkali. Although the aldehyde could be obtained by dehydrogenation of ethyl alcohol, the Germans, in their plant at Schkopau, prepared it from acetylene by absorption in sulphuric acid using mercuric sulphate and iron sulphate as catalysts.

At Schkopau the aldol was reduced to 1,3-butylene glycol in copper reactors over a copper-chromite catalyst at a hydrogen pressure of 300 atm. and a temperature of 60° to 85° C. Dehydration of the glycol was brought about by passage with steam over a sodium acid pyrophosphate catalyst ($Na_2H_2P_2O_7$) at 270° C. The reactions involved in this method are:

$$2CH_3CHO \longrightarrow \underset{\text{Adol}}{CH_3.CH.(OH).CH_2.CHO}$$

$$CH_3.CH(OH)CH_2CHO+H_2 \longrightarrow \underset{\text{1, 3-Butylene glycol}}{CH_3CH(OH)CH_2CH_2OH}$$

$$CH_3CH(OH)CH_2CH_2OH \longrightarrow CH_2{=}CH{-}CH{=}CH_2.$$

A more direct method from ethyl alcohol was devised by Lebedev [60, 1930], and this process was used on a wide scale both in Russia and the United States. Although most of the alcohol employed was from fermentation sources, yet since ethyl alcohol can readily be produced from ethylene, it is a possible route for the production of butadiene from petroleum. The process used in the United States was due to the Carbide and Chemicals Corporation. Although no technical details are available on this process, it is a modification of the Lebedev one which used a mixed aluminium-zinc oxide catalyst at 400° C. The estimate in 1943 was that approximately one-third of the butadiene made in the United States would be obtained from ethyl alcohol [30, 1943].

Another oxygen compound which has been suggested as an intermediate for the manufacture of butadiene is 2,3-butylene glycol, which is obtained by the selective fermentation of grain. The dehydration is most satisfactorily carried out by conversion to the diacetate and pyrolysis of the latter at 500° C.

The majority of the war production of butadiene in the United States was directly from petroleum sources. As stated previously, diolefines are formed to only a small extent in normal reforming operations. For high butadiene production the cracking temperature is increased and the pressure reduced, the required hydrocarbon being isolated from the C_4 fraction. Another important starting material for butadiene production was the butene-butane cut from reforming units or *n*-butane from natural gas or petroleum. In the case of *n*-butane, this is first dehydrogenated to butenes, which in turn are dehydrogenated to butadiene. The first stage, namely, dehydrogenation of butane, is carried out by passage over chromic oxide on alumina at 600° C., while the butene-butadiene step can be accomplished at 500° to 700° C. and 0·25 atm. pressure over zinc oxide or alumina catalyst coated with certain carriers [see 30, 1943].

Probably the most interesting process, from the organic chemists' point of view, for synthesizing butadiene is a novel one developed in Germany during the war [4, 1946]. The invention was due to Dr. Reppe, who was responsible for an entirely new field of acetylene chemistry. For the production of butadiene, acetylene is passed with aqueous formaldehyde over a copper-bismuth-acetylide catalyst supported on granular silica-gel at 5 atm. pressure and 90° to 110° C. to yield 1,4-butinediol.

$$C_2H_2+2HCHO \longrightarrow \underset{\text{1,4-Butinediol}}{HOCH_2C{:}C.CH_2OH}$$

The butinediol is then fully hydrogenated to the saturated glycol by means of a copper-nickel-manganese catalyst at 300 atm. at 120° C. Dehydration of the butanediol is effected by a sodium hydrogen phosphate-on-coke catalyst at 280° C. at atmospheric pressure.

Reactions of Diolefines with Halogens, Halogen Acids, and Hypohalous Acids

Since dienes possess two double bonds, they undergo many of the addition reactions which are also found with mono-olefines. Twice as much of the reagent reacts as for the mono-olefines, and the reaction takes place in a stepwise manner. For instance, one molecule of butadiene adds one molecule of halogen to give a dihalide; if excess of the halogen is present, the reaction proceeds further to give a tetrahalide, and here the reaction ceases.

It might be expected that the first step would take place at one double bond to give exclusively a 1,2-addition product.

$$CH_2{=}CH{-}CH_2{=}CH+Br_2 \longrightarrow CH_2Br{-}CHBr.CH{=}CH_2$$

$$CH_2{=}CH{-}CH{=}CH_2+HBr \longrightarrow CH_3CHBrCH{=}CH_2$$

This, however, is not the case since it has been shown that the product most usually obtained is formed by 1,4- and not 1,2-addition. Thus Farmer and his collaborators [27, 1928, 1929, 1930] have treated butadiene, the dimethyl butadienes, and cyclopentadiene dissolved in chloroform with bromine at −15° C. In all cases the predominant dibromide was that formed by 1,4-addition of the halogen to the hydrocarbon. With butadiene, the ratio of 1,4-dibromide to 1,2-dibromide was approximately 2 to 1. Farmer and Scott showed that with cyclopentadiene the proportion of the addition products was greatly affected by the solvent used, as shown in the following table:

Bromination of Cyclopentadiene

Solvent	*Temp. of reaction, °C.*	*% 1,4-*
Chloroform	−15	63·0
Hexane	−15	38·4
Acetic acid	+ 4	70·0
Carbon disulphide	−15	65·9

If an excess of the halogen is present, further addition occurs giving the tetrabromide. Many of the tetrabromides from conjugated dienes exist in two stereoisomeric forms. Reduction of these compounds with zinc and alcohol regenerates the diolefine.

A similar reaction occurs with hydrogen chloride as with the halogens. Thus Kharasch, Kritschevski, and Mayo [55, 1937] have shown that hydrogen chloride adds to butadiene to give a mixture of 3-chlorobutene-1 by 1,2-addition and 1-chlorobutene-2 by 1,4-addition, in this case the former being formed in greater amount.

However, with hydrogen bromide the course of the addition is influenced by the presence or absence of peroxides or oxygen. At −80° C. in the presence of antioxidants, the principal product from hydrogen bromide and butadiene is 3-bromo-butene-1 formed by 1,2-addition, but at higher temperatures in the presence of oxygen, the product obtained is crotyl bromide, which is the 1,4- addition product.

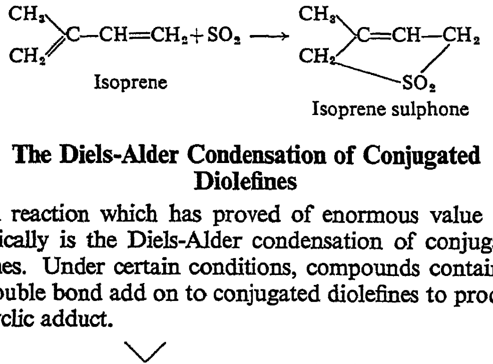
If two molecular proportions of halogen acid are employed for each molecule of diolefine, the dihydrohalide is formed. The compounds formed with isoprene and hydrogen bromide or hydrogen chloride have the formula $(CH_3)_2CX.CH_2.CH_2X$, where X is Br or Cl.

Hypochlorous and hypobromous acids add on to dienes in the same manner as the above to give mono- and dihalohydrins. The mono-compounds are again those mainly formed by 1,4-addition.

Reactions of Diolefines with Sulphur Dioxide

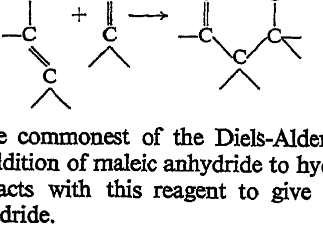
Sulphur dioxide reacts with diolefines in two ways. The first produces long-chain polymeric compounds while the second yields monomolecular cyclic sulphones. The latter in many cases are crystalline compounds which can be used for the purification of the hydrocarbons. Heating the sulphones above their melting-points brings about decomposition and yields the original diolefine.

An excellent example of monomeric sulphone formation is given by the C_5 diolefine, isoprene. This hydrocarbon can be prepared in the laboratory by the cracking of a hydrocarbon such as dipentene in an isoprene lamp. The crude isoprene obtained by this method is impure, and the most satisfactory method for obtaining the pure diene is by conversion into the monomeric sulphone, crystallization of the latter, and regeneration by heating above 120° C. The melting-point of isoprene sulphone is 63° to 63·5° C. The formation of these compounds again takes place by 1,4-addition.

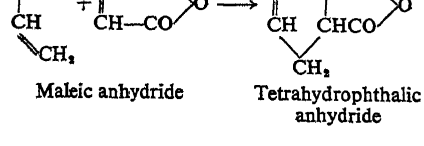


The Diels-Alder Condensation of Conjugated Diolefines

A reaction which has proved of enormous value synthetically is the Diels-Alder condensation of conjugated dienes. Under certain conditions, compounds containing a double bond add on to conjugated diolefines to produce a cyclic adduct.

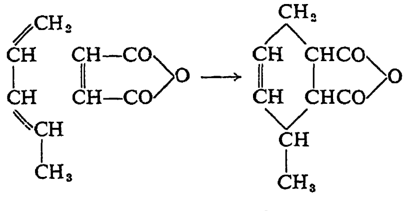


Perhaps the commonest of the Diels-Alder condensations is the addition of maleic anhydride to hydrocarbons. Butadiene reacts with this reagent to give tetrahydrophthalic anhydride.

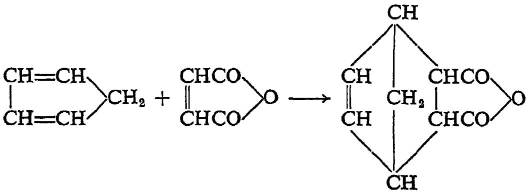


This compound is a crystalline material having a melting-point of 103° to 104° C. The other dienes such as isoprene and cyclopentadiene also form crystalline adducts with maleic anhydride and these are extremely useful for identification purposes.

In all these condensation reactions it will be noticed that the addition occurs in the 1,4-position. An interesting point concerning the addition of maleic anhydride to piperylene was demonstrated by Craig [10, 1943]. Piperylene, which is 1,3-pentadiene, can exist in *cis* and *trans* forms and Craig showed that although *trans*-piperylene reacts in the normal way, producing a methyltetrahydrophthalic anhydride,

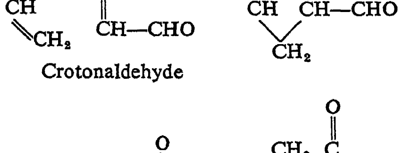


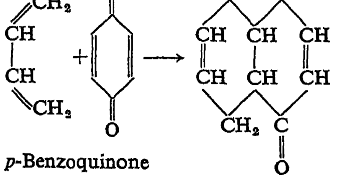
the *cis*-isomer forms no condensation product but undergoes polymerization. Cyclopentadiene reacts extremely readily with maleic anhydride to give a compound having a bicyclic structure.

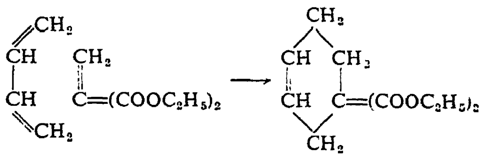


The reaction of butadiene with maleic anhydride has been used as the basis of a method for estimating this hydrocarbon in mixture with mono-olefines and paraffins. The C_4 cut from thermal reforming operations contains all the C_4 mono-olefines, paraffins, and butadiene. Treatment with maleic anhydride at 100° C. brings about condensation between the butadiene and anhydride and leaves the olefines and paraffins unaffected.

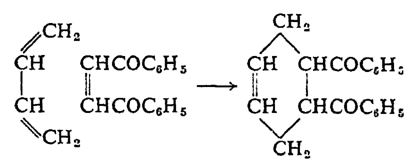
The known examples of the Diels-Alder condensation are far too numerous to enumerate in this article. A most exhaustive survey of the various types of reactants which undergo condensation is given in a review by Norton [75, 1942]. The generality of the reaction is shown by the addition of crotonaldehyde, methylenemalonic ester, *p*-benzoquinone, and dibenzoylethylene to butadiene. The reactions which take place are expressed as follows:





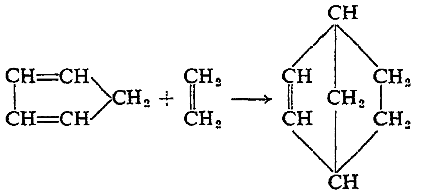


Methylene malonic ester



Dibenzoylethylene

An interesting use of the condensation has recently been made in the synthesis of bicyclic hydrocarbons [46, 1941; 91, 1944]. Cyclopentadiene was heated under pressure in an autoclave with ethylene. Condensation between the two hydrocarbons took place to produce a solid hydrocarbon melting at 46° C. and boiling at 96·1° C. This was bicyclo-(2,2,1)-2-heptene, which on hydrogenation gave the fully saturated bicyclic naphthene.

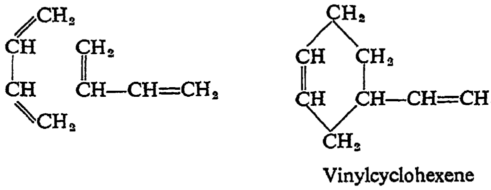


Bicyclo-(2,2,1)-2-heptene

Polymerization of Conjugated Diolefines

The most important commercial polymers from the diolefines are undoubtedly the synthetic rubbers. Buna S, an elastomer from butadiene and styrene, formed by far the greater proportion of the synthetic rubber programme in the United States during the recent war. Since synthetic rubber production is outside the scope of this article, the polymers which are to be discussed are the low molecular weight dimers and trimers.

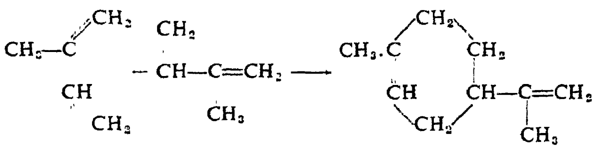
If butadiene is passed through a tube at 300° to 400° C. a liquid dimer is produced. This dimer, which is vinylcyclohexene, does not undergo further polymerization. It will be seen that, as with the Diels-Alder synthesis, the condensation takes place by 1,4-addition.



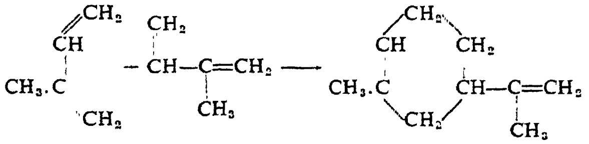
Vinylcyclohexene

Dehydrogenation of this polymer gives styrene or ethylbenzene. An interesting fact is that no open-chain dimers are formed.

In the same way, if isoprene is heated in the absence of oxygen or peroxides, a liquid dimer is produced instead of the usual rubber-like polymer. This liquid polymer appears to be a mixture of two cyclic olefines, limonene and *m*-menthadiene, both formed by 1,4-addition of two isoprene molecules.

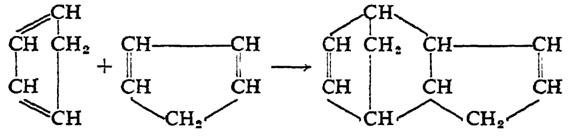


Limonene



m-Menthadiene

Cyclopentadiene polymerizes with extreme readiness to produce solid polymers. The dimer, dicyclopentadiene, is a crystalline solid which exists in two stereoisomeric forms. The reaction is reversible, since if dicyclopentadiene is heated to 160° to 170° C., particularly in the presence of iron wool, depolymerization takes place and cyclopentadiene distils off. The dicyclopentadiene is formed by the 1,4-addition of two cyclopentadiene molecules to produce a compound having a methylene bridge across the ring.



Dicyclopentadiene

A review of the formation and properties of the polymers of cyclopentadiene has recently been given in an article by Wilson and Wells [100, 1944].

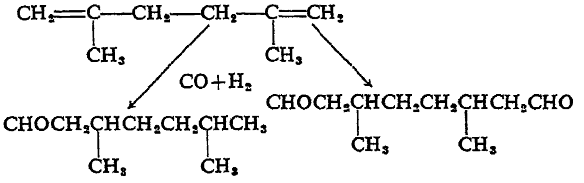
The Reactions of Diolefines with Hydrogen and Carbon Monoxide

The OXO reaction of Roelen gives exclusively monoaldehydes with conjugated diolefines, the other double bond becoming saturated by the addition of hydrogen. For instance, butadiene gives butan-1-al.

$$CH_2{=}CH{-}CH{=}CH_2+CO+2H_2 \longrightarrow CH_3CH_2CH_2CH_2CHO$$

Butan-1-al

Unconjugated diolefines have been shown to give a certain amount of the dialdehyde, 2,5-dimethylhexa-1,5-diene reacting under the OXO conditions to give 40% of dimethylhexandial, but the majority of the product is a monoaldehyde.



Reaction of Butadiene with Benzene

Ipatieff and co-workers [44*b*, 1944] showed that, using an excess of the aromatic, it was possible to alkylate benzene with butadiene using either 96% sulphuric acid or hydrogen fluoride as catalyst. The product of the reaction identified was 1,2-diphenylbutane, this being produced in 14% and 59% yield, on the basis of the benzene reacted, from sulphuric acid and hydrogen fluoride respectively. The postulated mechanism of the reaction was the preliminary formation of 1-phenyl-butene-2 by 1,4-addition followed by further reaction of this olefine with benzene.

Reaction of Butadiene with Ozone

Butadiene reacts with ozone to give a mono-ozonide and a diozonide [83, 1940]. The former is produced when ozone is passed into a solution of butadiene in petroleum ether. This compound, which was shown to be formed by 1,3-addition, separates out as a white amorphous solid. The diozonide which is formed by complete ozonization in chloroform solution is soluble in chloroform. Owing to its highly explosive nature, great difficulty was experienced in isolating it. The structure of the diozonide showed it to have been formed by 1,2-, 3,4-addition.

REFERENCES

1. Armstrong, R. T., Little, J. R., and Doak, K. W. *Ind. Eng. Chem.* 36, 628 (1944).
2. Beckham, L. J. U.S. Pat. 2,265,993 (16 Dec. 1942); U.S. Pat. 2,343,362 (7 Mar. 1944); U.S. Pat. 2,354,359 (25 July 1944).
3. Berg, L., Summer, G. L., and Montgomery, C. W. *Ind. Eng. Chem.* **38**, 734 (1946).
4. B.I.O.S. Final Report No. 367, *Manufacture of 1,4 Butinediol at I.G. Ludwigshafen.* H.M. Stationery Office, London (1946).
5. Bond, jnr., G.R. Paper presented before the Petroleum Division of the A.C.S., Chicago Meeting, Sept. 1946.
6. Brain, G. *J. Am. Chem. Soc.* **51**, 228 (1929).
7. Byrnes, A. C., and Doumani, T. F. *Ind. Eng. Chem.* **35**, 349 (1943).
8. Calcott, W. S., Tinker, J. M., and Weinmayr, V. J. *J. Am. Chem. Soc.* **61**, 1010 (1939).
9. C.I.O.S. Report, Item 22, File No. XXVI-2, *Synthetic Emulsifying Agents, Wetting Agents, Detergents and Soap Substitutes.* H.M. Stationery Office, London (1946).
10. Craig, D. *J. Am. Chem. Soc.* **65**, 1006 (1943).
11. Criegee, R. *Ann.* **481**, 263 (1930).
12. Criegee, R., Pitz, H., and Flygan, H. *Ber.* **72**, 1799 (1939).
13. Cunneen, J. I. *J. Chem. Soc.* 36 (1947).
14. Demjanov, N. Ya. *J. Russ. Phys. Chem. Soc.* **36**, 15 (1904).
15. Dermer, O. C., and Dysinger, G. A. *J. Am. Chem. Soc.* **61**, 750 (1939).
16. Edlund, K. R., and Evans, T. W. U.S. Pat. 2,006,734 (2 July 1935).
17. ——— —— U.S. Pat. 2,042,218 (26 May 1936).
18. Egloff, G., Hulla, G., and Komarewsky, V. I. *Isomerisation of Pure Hydrocarbons.* A.C.S. Monograph, No. 88 (1942).
19. Egloff, G., Morrell, J. C., Thomas, C. L., and Bloch, H. S. *J. Am. Chem. Soc.* **61**, 3571 (1939).
20. Egloff, G., and Hulla, G. *Chem. Reviews*, **35**, 279 (1944); ibid. **36**, 63 (1945).
21. Elder, A. L. *Ind. Eng. Chem.* **34**, 1260 (1942).
22. Ellis, C. *The Chemistry of Petroleum Derivatives,* (*a*) vol. **1** (1934); (*b*) vol. **2** (1937).
23. Evans, T. W., Edlund, K. R., and Taylor, M. D. *Ind. Eng. Chem.* **30**, 55 (1938).
24. Evans, T. W., and Edlund, K. R. *Ind. Eng. Chem.* **28**, 1186 (1936).
25. ——— —— U.S. Pat. 2,051,473 (18 Aug. 1936).
26. Farmer, E. H., and Thorpe, J. F. 'The Chemistry of Hydrocarbons', *Science of Petroleum*, vol. 2 (1938).
27. Farmer, E. H., Lawrence, C. D., and Thorpe, J. F. *J. Chem. Soc.* 729 (1928); Farmer, E. H., and Scott, W. D., ibid. 172 (1929); Farmer, E. H., Lawrence, C. D., and Scott, W. D., ibid. 510 (1930).
28. Farmer, E. H., and Sundralingham, A. *J. Chem. Soc.* 121 (1942).
29. Freeth, F. A. *Chemical Trade J.* **119**, 365 (1946).
30. Frolich, P. K., and Morrell, C. E. *Chem. Eng. News,* **21**, 1138 (1943).
31. Hardy, D. V. N. *J. Chem. Soc.* 364 (1936).
32. Harries, C. D. *Ann.* **343**, 311 (1905).
33. Hartig, M. J., Hughes, E. C., and Veatch, F. Paper presented before the Petroleum Division of the A.C.S., Atlantic City Meeting, April 1946.
34. Hay, R. G., Montgomery, C. W., and Coull, J. *Ind. Eng. Chem.* **37**, 335 (1945).
35. Hickinbottom, W. J. *J. Chem. Soc.* 2400 (1932); 319 (1934); 1279 (1935).
36. Hoffmann, K. A., Erhardt, O., and Schneider, O. *J. Am. Chem. Soc.* **46**, 657 (1913).
37. Hugel, G., and Krassilchick, A. *J. Inst. Pet.* **15**, 744 (1929).
38. Hurd, C. D., and Goldsby, A. R. *J. Am. Chem. Soc.* **56**, 1812 (1934).
39. Ipatieff, V. N., Pines, H., and Friedman, B. S. *J. Am. Chem. Soc.* **60**, 2495 (1938).
40. Ipatieff, V. N. U.S. Pat. 2,046,900 (7 July 1936).
41. Ipatieff, V. N., and Pines, H. *J. Org. Chem.* **1**, 464 (1936).
42. Ipatieff, V. N., Pines, H., and Friedman, B. S. *J. Am. Chem. Soc.* **60**, 2731 (1938).
43. Ipatieff, V. N., and Friedman, B. S. *J. Am. Chem. Soc.* **61**, 71 (1939).
44. Ipatieff, V. N., Pines, H., and Schaad, R. E. (*a*) *J. Am. Chem. Soc.* **56**, 2696 (1934); (*b*) ibid. **66**, 816 (1944).
45. Jones, S. O., and Reid, E. E. *J. Am. Chem. Soc.* **60**, 2452 (1938).
46. Joshel, L., and Butz, L. *J. Am. Chem. Soc.* **63**, 3350 (1941).
47. Kelly, R. N. *Chem. Reviews*, **28**, 229 (1941).
48. Kharasch, M. S., May, E. M., and Mayo, F. R. *J. Org. Chem.* **3**, 175 (1938).
49. Kharasch, M. S., Jensen, E. V., and Urry, W. H. *Science*, **102**, 128 (1945).
50. ——— ——— ——— *J. Am. Chem. Soc.* **67**, 1626 (1945).
51. ——— ——— ——— *J. Am. Chem. Soc.* **67**, 1864 (1945).
52. ——— ——— ——— *J. Am. Chem. Soc.* **68**, 154 (1946).
53. Kharasch, M. S., Seyler, R. C., and Mayo, F. R. *J. Am. Chem. Soc.* **60**, 882 (1938).
54. Kharasch, M. S., and Ashford, T. A. *J. Am. Chem. Soc.* **58**, 1733 (1936).
55. Kharasch, M. S., Kritschevski, J., and Mayo, F. R. *J. Org. Chem.* **2**, 489 (1937).
56. Kistiakowsky, G. B., and Smith, W. R. *J. Am. Chem. Soc.* **58**, 766 (1936).
57. Kondakow, J. T. *Russ. Phys. Chem. Soc.* **28**, 12 (1894).
58. Krapivin, S. *Bull. Soc. Imp. Nat. Moscow*, **1** (1908).
59. Krassilchick, A. *J. Inst. Pet.* **22**, 44 (1936).
60. Lebedev, S. V. Brit. Pat. 331,482 (30 June 1930).
61. Levy, N., Scaife, C. W., and Smith, A. E. W. *J. Chem. Soc.* 1083, 1096, 1100 (1946).
62. Markovnikoff, V. *Ann.* **153**, 256 (1870).
63. Mayo, F. R., and Walling, C. *Chem. Reviews*, **27**, 351 (1940).
64. McCubbin, R. J., and Adkins, H. *J. Am. Chem. Soc.* **52**, 2547 (1930).
65. Michael, A., and Carlson, G. H. *J. Org. Chem.* **5**, 1 (1940).
66. ——— —— *J. Am. Chem. Soc.* **59**, 843 (1937).
67. ——— —— *J. Am. Chem. Soc.* **57**, 1268 (1935).
68. Milas, N. A., and Sussman, S. *J. Am. Chem. Soc.* **58**, 1302 (1936).
69. Milas, N. A. *J. Am. Chem. Soc.* **59**, 2343 (1937).
70. Milas, N. A., and Sussman, S. *J. Am. Chem. Soc.* **59**, 2345 (1937).
71. Morton, A. A., Brown, M. L., Holden, M. E. I., Letsinger, R. L., and Magat, E. E. *J. Am. Chem. Soc.* **67**, 2224 (1945).
72. Nametkin, S. T., and Abakumovskya, L. N. *J. Gen. Chem.* **6** (1936).
73. Natelson, S. *J. Am. Chem. Soc.* **56**, 1583 (1934).
74. Naylor, R. F. *J. Chem. Soc.* 247 (1945).
75. Norton, J. A. *Chem. Reviews*, **31**, 319 (1942).
76. Ormandy, W. R., and Craven, E. C. *J. Inst. Pet.* **13**, 311 (1927); ibid. **13**, 844 (1927).
77. Riebsomer, J. L. *Chem. Reviews*, **36**, 157 (1945).
78. Schmidt, J. *Ber.* **36**, 1775 (1903).
79. Smith, J. C. *Annual Reports on the Progress of Chemistry for* 1939, issued by the Chemical Society, London.
80. Smith, R. A., and Rodden, C. J. *J. Am. Chem. Soc.* **59**, 2353 (1937).
81. Snow, R. D., and Frey, F. E. *Ind. Eng. Chem.* **30**, 176 (1938); *J. Am. Chem. Soc.* **65**, 2416 (1943).
82. Spaght, E. M. C.I.O.S. Report, Item 30, File No. XXXII-68, *The Manufacture and Application of Lubricants in Germany.* H.M. Stationery Office, London (1946).
83. Spencer, C. C., Weaver, W. J., Obberright, E. A., Symer, H. J., Barney, A. L., and Elder, A. L. *J. Org. Chem.* **5**, 610 (1940).
84. Spengler, G., and Moldner, R. *Oel und Kohle* (1944).
85. Sudborough, J. A. *Chem. Zentralblatt*, 794 (1891).

86. Suter, C. M., Evans, D. B., and Kiefer, J. M. *J. Am. Chem. Soc.* **60**, 538 (1938).
87. Suter, C. M., and Malkemus, J. D. *J. Am. Chem. Soc.* **63**, 978 (1941).
88. Suter, C. M., Malkemus, J. D., and Archer, S. *J. Am. Chem. Soc.* **63**, 1594 (1941).
89. Swern, D., Billen, G. N., and Scanlan, J. T. *J. Am. Chem. Soc.* **68**, 1504 (1946).
90. Teter, J. N., Olson, L. E., and Ries, H. E., jnr. Paper presented before the Petroleum Division of the A.C.S., Atlantic City Meeting (April 1946).
91. Thomas, C. L. *Ind. Eng. Chem.* **36**, 1 (1944).
92. Tilden, W. A., and Forster, M. O. *J. Chem. Soc.* 324 (1894).
93. Vaughan, W. E., and Rust, F. F. U.S. Pat. 2,398,481 (16 Apr. 1946).
94. —— —— U.S. Pat. 2,411,983 (3 Dec. 1946).
95. —— —— *J. Org. Chem.* **5**, 472 (1940).
96. Waters, W. A. *Annual Reports on the Progress of Chemistry for 1945.* Issued by the Chemical Society, London.
97. Weitzel, R. G.P. 479,079 (4 Apr. 1925).
98. Westlake, H. E., jnr., Mayberry, M. G., Whitlock, M. H., West, I. R., and Haddad, G. J. *J. Am. Chem. Soc.* **68**, 748 (1946).
99. Whitmore, F. C., and Church, J. M. *J. Am. Chem. Soc.* **54**, 3710 (1932).
100. Wilson, P. J., jnr., and Wells, J. H. *Chem. Reviews*, **34**, 1 (1944).
101. Wood, J. L. 'Reactions of Thiocyanogen', *Organic Reactions*, vol. 3 (1946).

MECHANISM OF ORGANIC REACTIONS

By F. C. WHITMORE and N. C. COOK

Penn. State College

A COMMON basis for reaction mechanisms can be found in an electronic approach. For such treatment the basic concepts of atomic and molecular structure must be borne in mind.

Atoms are composed of a nucleus surrounded by electrons. The nucleus is approximately 1/100,000 of the diameter of the atom, but so dense that it is practically the whole mass. The electrons surrounding the nucleus constitute essentially the entire atomic volume and are numerically equal to the atomic number.

As the atomic number of the chemical elements ascends from the lightest to the heaviest element, the positive charge on the nucleus and the number of surrounding electrons increase accordingly. These electrons are shown by quantum mechanics to be built up into energy-levels [12, 1949], and only the electrons in the outermost levels determine the chemical and physical properties of the elements.

A systematic recurrence of chemical and physical properties as the elements increase in atomic weight indicates a systematic recurrence of the same number of electrons in the outer levels. This periodicity of the elements is particularly noticeable in the rare gas elements—helium, neon, argon, krypton, xenon, and radon. The rare gas elements, unlike the other elements of the Periodic Table, have no tendency to react with themselves or with other elements. Since chemical reactivity is associated only with the electrons of the outermost energy-levels, stable electronic configurations have been ascribed to the outer levels of the rare gases. These configurations, 2 for helium and 8 for the others—the pair and the octet—represent the master key to an understanding of chemical reactions [1, 1941].

Atoms which do not contain these configurations in their outer level tend to lose, gain, or share electrons in order to attain the stable configuration of the nearest rare gas. This tendency is so great that atoms of the same elements often combine in order to share electrons and thereby obtain a more stable configuration. These binding forces are very strong in some cases as shown by the inertness of the nitrogen molecule, the heat generated when atomic hydrogen combines to form molecular hydrogen, and the inertness of molecular hydrogen with molecular chlorine unless some catalyst is used which is capable of creating atomic hydrogen or chlorine.

There are two chief ways in which atoms react to obtain stable configurations:

1. By sharing electrons, atoms are able to establish stable electronic configurations giving rise to neutral molecules known as non-electrolytes with little or no charge on the individual atoms.
2. By a process of gain and loss of electrons two elements can also establish stable configurations. The elements which build up stable configurations acquire negative charges and those which are stripped down to a stable configuration acquire positive charges. The products of such reactions are not molecules but charged atoms known as ions, and belong to a general class of compounds known as electrolytes.

The molecules of organic compounds are held together principally by bonds of the first type, i.e. shared electrons or the covalent bond.

It has been possible to determine the exact character of only the simplest molecule, hydrogen. G. N. Lewis [9, 1923], however, observed empirically that almost all of the facts of chemical bonding can be interpreted if one supposes that each valence link is formed by a *pair* of electrons shared between the linked atoms. And in practically all stable molecules of the lighter elements, the total number of valence electrons, shared or unshared, assignable to each atom has a definite value: 2 or 8, the pair or the octet.

The electrons of the shared bond are concentrated in a line joining the nuclei of the atoms they bond. They are not fixed in position but on the average assume a probable position about the axis.

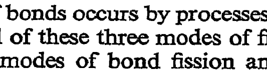
In a molecule such as ethylene, where the atoms are held together by two pairs of electrons, it is believed that one pair constitutes a bond almost identical with the single bond. The other pair, known as the π-electrons, assumes an orbital position about the axis of the single bond such as to give a band-like character to the double bond [11, 1946]. As will be shown later, the π-electrons are especially susceptible to attack by reagents needing either one or two electrons.

The molecule of the typical organic compound is a stable structure surrounded by electrical fields of electron pairs which are effective walls of defence against reaction. The problem of the chemist is to find reagents which will attack weak points in the various molecular structures and upset their 'stable' configuration. The atoms of the unstable molecules then readjust themselves until they find other electronic configurations which are stable to the new environment.

Since it is only the electrons which enter into reactions it is possible to treat reaction mechanisms through electronic concepts and arrive at generalized considerations that permit correlation of results which otherwise appear to be anomalous.

An exact treatment of an electronic approach would probably be in the realm of quantum mechanisms. However, there is much to be gained from an empirical approach based simply on the observations made by Lewis concerning the relationship of chemical bonding and stability to the pair and the octet of electrons.

By simply drawing all the ways in which the chemical bond of the molecule R:X can break, we have exactly the three ways in which such bonds do break.



The creation of bonds occurs by processes which are essentially a reversal of these three modes of fission.

These three modes of bond fission and bond creation serve as a basis for treating the mechanism of organic reactions. They are classified as (1) atom and free radical reactions; (2) carbonium ion or acidic reaction; and (3) carbanion or basic reaction.

Atom and Free Radical Reactions

The driving-force of these reactions lies in the single electron deficiency of a neutral atom or free radical. Examples are to be found in some of our most common reactions.

Atomic hydrogen reacts to produce molecular hydrogen:

$$\mathrm{H}\cdot+\mathrm{H}\cdot \quad \mathrm{H}:\mathrm{H}$$

Atomic chlorine reacts to produce molecular chlorine:

$$:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}\cdot+:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}\cdot \longrightarrow :\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}:$$

Molecular hydrogen does not react with molecular chlorine. If, however, some reagent, such as ultra-violet light, a sodium atom, or heat is brought into the mixture, reaction then takes place. Such reagents create atomic chlorine or hydrogen from the less reactive molecular form [3*a*, 1940].

$$\mathrm{Cl_2}+h\nu \longrightarrow 2:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}\cdot$$

$$\mathrm{Cl_2}+\mathrm{Na}\cdot \longrightarrow \mathrm{NaCl}+:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}\cdot$$

$$:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}\cdot+\mathrm{H_2} \longrightarrow \mathrm{H}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}:+\mathrm{H}\cdot$$

$$\mathrm{H}\cdot+\mathrm{Cl_2} \longrightarrow \mathrm{H}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}:+:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}\cdot$$

The molecular equivalents of the elemental atoms are the free radicals. The methods for their generation and the character of their reactions are similar to those for atoms but are modified by the factors which influence molecular structure. An inspection of the structural character of the simple methyl radical is worth while. A carbon atom has four electrons in the outermost level. In a neutral methyl radical $\mathrm{H}:\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}\cdot$, three of the electrons have been shared with hydrogen atoms, leaving one odd electron. This is an unstable arrangement in much the same way as a chlorine atom, $:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}\cdot$, is unstable. Similarly, an unstable arrangement is present in any organic molecule containing an atom with only seven electrons, one being unpaired.

Evidence is abundant for the existence of free radicals and for the character of their reactions. Tetramethyllead passed through a hot tube at temperatures $> 400°$ C. decomposes. The electron pair bonding the lead and carbon is broken so as to give neutral methyl radicals, $\mathrm{H}:\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}\cdot$, and lead, $\cdot\overset{\cdot}{\underset{\cdot}{\mathrm{Pb}}}\cdot$. The lead is deposited as a metallic mirror at the zone of decomposition. If a lead deposit is placed on the cooler wall of the tube just beyond the hot zone of decomposition, the methyl radicals react with the lead to remove the deposit and again form tetramethyllead [10, 1929]. Thermal cracking of ethane also generates methyl radicals, but at a higher temperature, $> 750°$ C. Here again, proof can be established by the removal of metallic mirrors and the identification of the metal alkyls.

There are many methods of creating free radicals other than by thermal rupture of the electron pair. The most widely used method is generation from peroxides which break down at ordinary temperature or under mild ultra-violet radiation to generate free radicals.

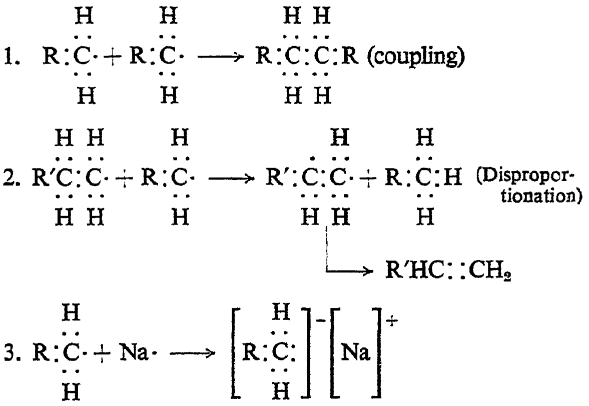
$$\mathrm{(RCOO)_2} \rightleftharpoons 2\mathrm{RCOO}\cdot \xrightarrow{\Delta} \mathrm{R}\cdot+\mathrm{CO_2}$$

In addition to speeding up the decomposition of peroxides, ultra-violet light generates free radicals from aldehydes, ketones, diketones, &c. The use of elements such as sodium will also generate free radicals and thus bring about free radical reactions [5, 1933].

There are few graphic demonstrations such as the removal of metallic mirrors for the identification of the majority of free radical reactions which take place in solutions. However, their presence can be shown just as conclusively. The most commonly used identifications for free radical mechanisms are the highly characteristic reactions which they undergo, and their dependence upon known free radical catalysts for initiation.

It is interesting to note the various ways in which free radicals react:

With Radicals and Atoms

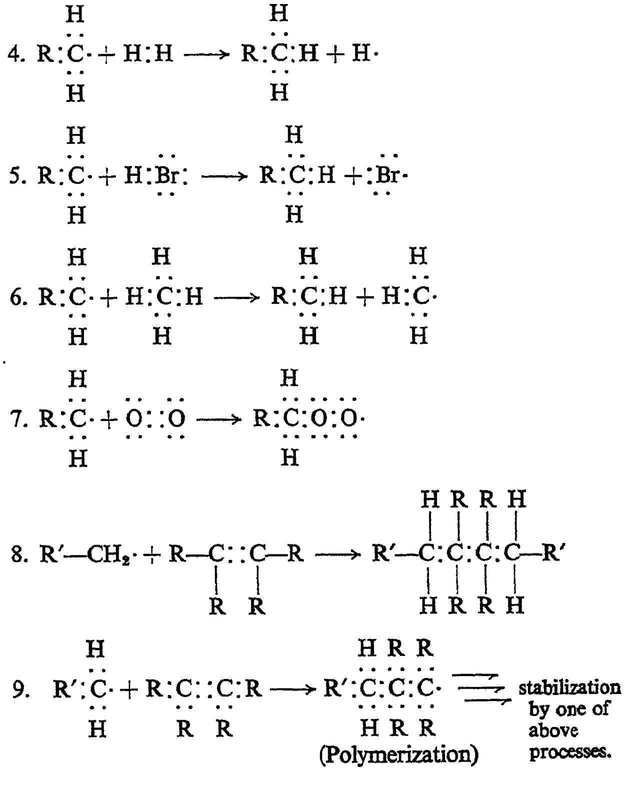


1. $\mathrm{R}:\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}\cdot+\mathrm{R}:\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}\cdot \longrightarrow \mathrm{R}:\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}:\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}:\mathrm{R}$ (coupling)

2. $\mathrm{R'}\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}:\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}\cdot+\mathrm{R}:\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}\cdot \longrightarrow \mathrm{R'}:\overset{\cdot}{\underset{\mathrm{H}}{\mathrm{C}}}:\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}\cdot+\mathrm{R}:\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}:\mathrm{H}$ (Disproportionation)
   $\longrightarrow \mathrm{R'HC::CH_2}$

3. $\mathrm{R}:\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}\cdot+\mathrm{Na}\cdot \longrightarrow \left[\mathrm{R}:\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}:\right]^-\left[\mathrm{Na}\right]^+$

With Molecules



4. $\mathrm{R}:\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}\cdot+\mathrm{H}:\mathrm{H} \longrightarrow \mathrm{R}:\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}:\mathrm{H}+\mathrm{H}\cdot$

5. $\mathrm{R}:\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}\cdot+\mathrm{H}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Br}}}: \longrightarrow \mathrm{R}:\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}:\mathrm{H}+:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Br}}}\cdot$

6. $\mathrm{R}:\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}\cdot+\mathrm{H}:\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}:\mathrm{H} \longrightarrow \mathrm{R}:\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}:\mathrm{H}+\mathrm{H}:\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}\cdot$

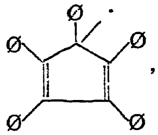
7. $\mathrm{R}:\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}\cdot+\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{O}}}::\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{O}}} \longrightarrow \mathrm{R}:\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{O}}}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{O}}}\cdot$

8. $\mathrm{R'}\text{—}\mathrm{CH_2}\cdot+\mathrm{R}\text{—}\underset{\mathrm{R}}{\mathrm{C}}::\underset{\mathrm{R}}{\mathrm{C}}\text{—}\mathrm{R} \longrightarrow \mathrm{R'}\text{—}\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}:\overset{\mathrm{R}}{\underset{\mathrm{R}}{\mathrm{C}}}:\overset{\mathrm{R}}{\underset{\mathrm{R}}{\mathrm{C}}}:\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}\text{—}\mathrm{R'}$

9. $\mathrm{R'}:\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}\cdot+\mathrm{R}:\underset{\mathrm{R}}{\mathrm{C}}::\underset{\mathrm{R}}{\mathrm{C}}:\mathrm{R} \longrightarrow \mathrm{R'}:\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}:\overset{\mathrm{R}}{\underset{\mathrm{R}}{\mathrm{C}}}:\overset{\mathrm{R}}{\underset{\mathrm{R}}{\mathrm{C}}}\cdot \rightleftharpoons$ stabilization by one of above processes.
   (Polymerization)

Many free radicals can undergo all the reactions as outlined above. But free radicals are similar to other reagents of attack in that they do the easiest thing to relieve their instability. This accounts for the high degree of selectivity observed when the structure of the radical and the environment are changed.

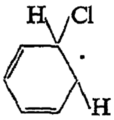
From the property of alkyl radicals to remove metal mirrors it has been possible to determine the half-life of a methyl radical, which is probably the most reactive radical, as 0·001 to 0·01 sec. [3*b*, 1940]. At the other extreme is the stability of such well-known free radicals as triphenylmethyl. Pentaphenylcyclopentadienyl radical, a



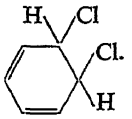
solid purple compound, is extremely stable. Whereas the methyl radical is unstable to an unusual degree and reacts quickly to relieve its deficiency, pentaphenylcyclopentadienyl radical finds itself capable of supplying its own needs by resonating the odd electron into a series of positions all of which are equal and have a high degree of stability [8, 1937].

Kharasch has found that *tert.*-butyl and benzyl radicals are not sufficiently reactive to abstract a chlorine atom from carbon tetrachloride, whereas primary and secondary alkyl radicals will [9, 1923].

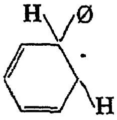
The tendency towards disproportionation is likewise related to the structure of the radical and to the environment. In the photohalogenation of benzene the radical



reacts with Cl_2 to give

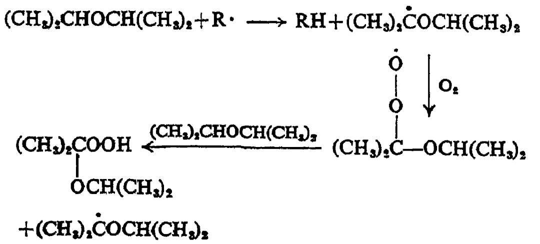


However,



does not react with the molecule (benzoyl peroxide) which generated the free radical, but only with an acyloxy radical to which it gives a hydrogen atom, thereby becoming biphenyl by disproportionation.

The course of many free radical reactions can be accounted for on the basis of attack to form the most stable free radical. This order of stability is tertiary >> secondary > primary, the opposite of their reactivity. Many reactions involving methylenic activity such as vapour-phase chlorination or peroxidation can be correlated on this basis. The high rate of peroxidation of tertiary olefines and paraffins can thus be accounted for. Diisopropyl ether, because of its tertiary character, forms peroxides much more readily than does diethyl or di-*n*-butylether.



$$(CH_3)_2CHOCH(CH_3)_2 + R\cdot \longrightarrow RH + (CH_3)_2\dot{C}OCH(CH_3)_2$$

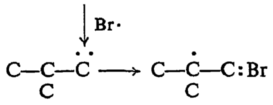
$$(CH_3)_2\dot{C}OCH(CH_3)_2 \xrightarrow{O_2} (CH_3)_2C(O\dot{O})OCH(CH_3)_2 \xrightarrow{(CH_3)_2CHOCH(CH_3)_2} (CH_3)_2C(OOH)OCH(CH_3)_2 + (CH_3)_2\dot{C}OCH(CH_3)_2$$

Peroxide Effect.

The addition of hydrogen bromide to olefinic double bonds under ionic conditions takes place as expected. The π-electrons are usually displaced toward the least crowded atom and are captured by a proton. The only remaining position for the bromide ion is the more crowded deficient carbon. Peroxides reverse this mode of addition. The decomposition of the peroxide generates a free radical which reacts with the hydrogen bromide.

$$R\cdot + HBr \longrightarrow RH + Br\cdot$$

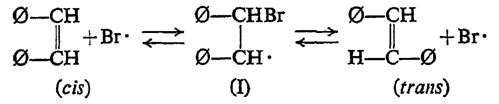
The neutral bromine atom attacks the π-electrons in the vicinity of the least crowded carbon atom, leaving the odd electron for the other carbon:



$$\underset{C}{C{-}C{-}\ddot{C}} \;(+\,Br\cdot) \longrightarrow \underset{C}{C{-}\dot{C}{-}C{:}Br}$$

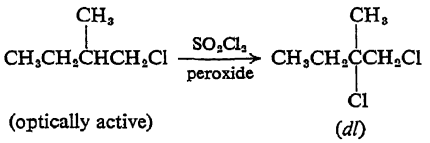
Thus the only place for the hydrogen atom to go is to the more highly branched carbon.

The configurational nature of the free radical is partly shown by the following reactions:



$$\begin{matrix}Ø{-}CH\\ \|\\ Ø{-}CH\end{matrix} + Br\cdot \rightleftarrows \begin{matrix}Ø{-}CHBr\\ |\\ Ø{-}CH\cdot\end{matrix} \rightleftarrows \begin{matrix}Ø{-}CH\\ \|\\ H{-}C{-}Ø\end{matrix} + Br\cdot$$

Kharasch [8, 1937] has shown that such a radical as (I) would be configurationally unstable. Also the free radical replacement of the tertiary hydrogen in active amyl chloride appears to result in complete loss of optical activity [11, 1946]:



$$CH_3CH_2\overset{CH_3}{\overset{|}{C}}HCH_2Cl \xrightarrow[\text{peroxide}]{SO_2Cl_2} CH_3CH_2\underset{Cl}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}CH_2Cl$$

Polymerization Reactions [11*b*, 1946].

By the proper selection of molecular structures and conditions, free radicals can be made to undergo addition reactions which give long chains before their growth is interrupted. In this type of reaction an initiating radical or atom attaches itself to the more exposed olefinic carbon of an unsaturated molecule by capturing one of the π-electrons. The odd electron left on the adjacent carbon creates a new deficiency which reacts similarly with another unsaturated molecule to give a still larger free radical. The molecule continues to grow by this chain-type reaction until it finds some way of satisfying its deficiency, without creating another in the same molecule.

It is possible to control free radical polymerization to an unusual degree by limiting the number of initiating reactions, selecting molecules which do not readily undergo side reactions such as disproportionation, making proper choice of concentration, solvent, inhibitors, chain stoppers, and transfer reagents. The use of monomer mixtures adds still another variation to these reactions.

The products of these reactions are high molecular weight polymers of unusual, varied, and useful properties. These reactions have probably received a more thorough investigation and application than any other similar study in the last 20 years.

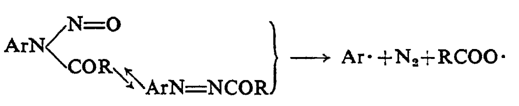
It is helpful to consider the steps in radical polymerization as initiation, propagation, and cessation.

$$R\cdot+M \longrightarrow RM\cdot \rightleftharpoons RM_n^{\cdot} \longrightarrow RM_n$$

(Initiation) (Propagation) (Cessation)

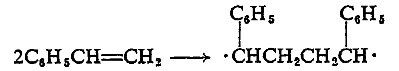
Initiation. Some of the molecules which enter into radical polymerization are styrene, butadiene, acrylates, vinyl chloride and acetate, vinylidine chloride, allyl esters and vinyl pyridine, all having readily available π-electrons. Catalysts for the initiation reactions include acyl peroxide, diazo compounds, alkyl peroxides, radicals from photolysis of aldehydes and ketones, free metals and metal from decomposition of metal alkyls.

By labelling the initiating radicals it has been possible to verify their presence in many polymer samples and thus prove their role as initiators. Selective reactivity of radicals can be studied in this same manner. Nitrosoanilides, which presumably generate an acyl and acyloxy radical simultaneously, always introduce only the acyl fragment into the polymer molecules, indicating that the acyloxy radical is far less effective as an initiating radical [11*c*, 1946].



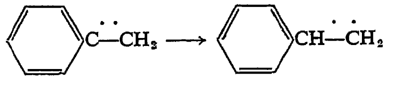
The acyloxy radical reacts with an available hydrogen atom, which the polymer molecules give up by disproportionation or chain transfer, and is always isolated as the acid.

It has been almost universally observed that the reactions involving catalysts of the above type proceed at a rate proportional to the square root of the catalyst concentration. This is in agreement with the observed first-order reaction rate for the decomposition of acyl peroxides and similar radical catalysts. Polymerizations which can be carried out without catalysts have been observed to be second-order reactions in respect to monomer concentration. This is readily accounted for if the initiation process is a bimolecular dimerization of the monomer as originally suggested by Staudinger.



$$2C_6H_5CH{=}CH_2 \longrightarrow \cdot\overset{C_6H_5}{\overset{|}{C}}HCH_2CH_2\overset{C_6H_5}{\overset{|}{C}}H\cdot$$

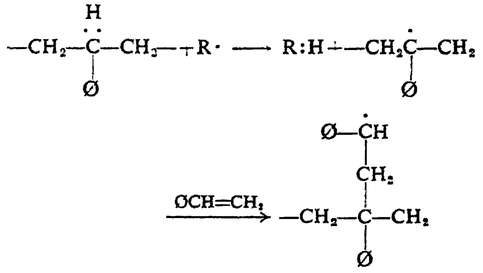
The initiating dimerization might be due to the tendency of the electron pair to localize an odd electron in the vicinity of the terminal carbons.



Dimerization could follow with a similar molecule and thus lead to formation of free radical polymers without the aid of an outside catalyst.

Propagation. The most important factor to be considered in the growth of polymer chains is the mode of addition. There is little evidence for any other type of addition except head to tail, which may be expected for several reasons: (1) The stability of free radicals is in the order tertiary >> secondary > primary. (2) Sterically a deficient carbon can attack a terminal position easier than an inside position. (3) The electrons are more apt to be in the vicinity of the terminal carbon than the inside carbon.

The symmetrical growth of the polymer molecule is not disturbed by intramolecular rearrangement (as in ionic polymerization), but may be affected by further reaction of functional groups along the chain, either within the molecule or with other polymer molecules. Since polystyrene and other polymers can easily be deprived of their tertiary hydrogen by other radicals, branched polymers result from chain-transfer reactions:



$$-CH_2-\underset{\O}{\underset{|}{\overset{H}{\overset{\cdot\cdot}{C}}}}-CH_2-+R\cdot \longrightarrow R{:}H+-CH_2\underset{\O}{\underset{|}{\overset{\cdot}{C}}}-CH_2$$

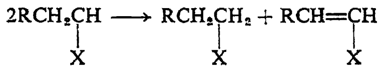
$$\xrightarrow{\O CH=CH_2} -CH_2-\underset{\O}{\underset{|}{\overset{\overset{\overset{\O-\dot{C}H}{|}}{CH_2}}{\overset{|}{C}}}}-CH_2$$

In contrast to most ionic reactions, free radical reactions are seldom reversible. This might be the result of some of the following factors: (1) exhaustion of the catalyst due to its entering into the reaction; (2) absence of weak spots for attack in products of the reaction; (3) non-occurrence of rearrangements in free radical reactions, indicating little tendency for a carbon deficient in only one electron to satisfy its needs by getting them from an adjacent carbon-to-carbon linkage. This, of course, only means that the molecule has easier ways of getting an electron, such as disproportionation or further propagation.

Under drastic conditions, however, some polymers can be forced into equilibrium reactions. Polystyrene at high temperature and with free radical catalysts reaches an equilibrium viscosity. Methyl methacrylate and methacrylate polymers readily yield monomer on thermal cracking.

Cessation. There are a number of ways in which an individual polymer chain may become stabilized. Reaction with another radical to couple or disproportionate may be regarded as normal cessation.

$$2R\cdot \longrightarrow R{:}R \quad \text{(coupling)}$$



$$2RCH_2\underset{X}{\underset{|}{C}}H \longrightarrow RCH_2\underset{X}{\underset{|}{C}}H_2 + RCH{=}\underset{X}{\underset{|}{C}}H$$

(disproportionation)

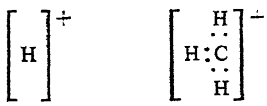
The latter seems to be more favoured when it can occur, i.e. when the radical has an active hydrogen atom on the β-carbon. Disproportionation of free radicals is similar to olefine formation in ionic polymerization. The ionic polymer loses a proton to its environment (acid medium) and produces a double bond, whereas the free radical loses a hydrogen atom to its environment (other free radicals) and likewise produces a double bond.

Discussion of all the intricacies of radical reactions, and particularly of radical polymerization, would require such detail as to obscure the main purpose of this treatment which is to show relationship between reaction mechanisms. For more complete treatments of these interesting reactions readers are referred to the excellent review by Hey and Waters in *Chemical Reviews* in 1937 and the book by C. C. Price, *Reactions at Carbon Carbon Double Bonds.*

Carbonium Ion or Acidic Reactions

The driving force of these reactions lies in the electron-pair deficiency of a carbon atom which has only three pairs of electrons instead of its stable quota of four pairs, and its reactions are those by which it can most easily acquire an electron pair.

In so far as a molecule can resemble an atom, the molecular carbonium ion has only one atomic equivalent—the proton—which it resembles by virtue of its deficiency of one pair.

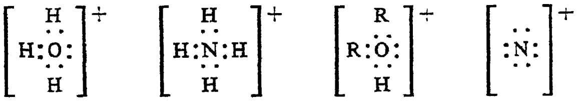


$$\left[\mathrm{H}\right]^{+} \qquad \left[\mathrm{H}:\overset{\mathrm{H}}{\underset{\mathrm{H}}{\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{C}}}}}\right]^{+}$$

The proton will not exist alone in any medium where it can attach itself to an electron pair. Thus it reacts with an unshared pair of electrons on the oxygen in H_2O to give H_3O^+ and on the nitrogen in NH_3 to give NH_4^+.

Accordingly a carbonium ion could not be expected to exist as a stable entity in any situation where it can relieve its deficiency.

An inspection of the electronic structure of the hydronium, ammonium, oxonium, and sodium ions reveals a basic difference between these stable ions and the proton and the carbonium ions. The ordinary ions have become such by acquiring a proton or losing electrons. The result is that all the atoms involved have the stable quota of electrons required by the G. N. Lewis pair and octet theory.



$$\left[\mathrm{H}:\overset{\mathrm{H}}{\underset{\mathrm{H}}{\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{O}}}}}:\right]^{+} \quad \left[\mathrm{H}:\overset{\mathrm{H}}{\underset{\mathrm{H}}{\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{N}}}}}:\mathrm{H}\right]^{+} \quad \left[\mathrm{R}:\overset{\mathrm{R}}{\underset{\mathrm{H}}{\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{O}}}}}:\right]^{+} \quad \left[:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{N}}}:\right]^{+}$$

The proton has no electrons but needs two. The carbonium ion has only six electrons but needs eight, and is consequently both unstable and reactive to an extraordinary degree. Ordinarily it simply cannot exist but must undergo an immediate stabilizing change. Some of the special conditions under which carbonium ions are stable offer convincing evidence for their existence.

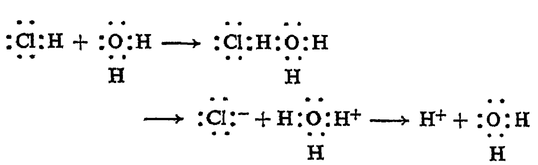
Triphenylcarbinol and concentrated sulphuric acid, both non-electrolytes, react to give a highly coloured conducting solution whose molecular freezing-point depression is four times that produced by a non-electrolyte [3*c*, 1940]. The reaction must be

$$(C_6H_5)_3COH + 2H_2SO_4 \longrightarrow (C_6H_5)_3C^+ + OH_3^+ + 2HSO_4^-.$$

Unlike benzoic acid which simply adds a proton, 2,4,6-trimethylbenzoic acid produces a fourfold freezing-point depression by virtue of the following reaction [3*c*, 1940]:

$$(CH_3)_3C_6H_2COOH + 2H_2SO_4 \longrightarrow (CH_3)_3C_6H_2CO^+ + OH_3^+ + 2HSO_4^-.$$

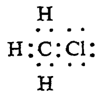
A word of explanation should be said about *ionization*, the process through which these reactions have occurred. The conversion of inert hydrogen chloride to reactive hydrochloric acid by solution in water is no longer regarded as a 'magical' influence of the latter. It may involve steps such as:



$$:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}:\mathrm{H} + :\overset{\cdot\cdot}{\underset{\underset{\mathrm{H}}{\cdot\cdot}}{\mathrm{O}}}:\mathrm{H} \longrightarrow :\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}:\mathrm{H}:\overset{\cdot\cdot}{\underset{\underset{\mathrm{H}}{\cdot\cdot}}{\mathrm{O}}}:\mathrm{H} \longrightarrow :\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}:^- + \mathrm{H}:\overset{\cdot\cdot}{\underset{\underset{\mathrm{H}}{\cdot\cdot}}{\mathrm{O}}}:\mathrm{H}^+ \longrightarrow \mathrm{H}^+ + :\overset{\cdot\cdot}{\underset{\underset{\mathrm{H}}{\cdot\cdot}}{\mathrm{O}}}:\mathrm{H}$$

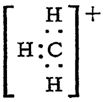
The initial step in the ionization may be an *addition* of the two molecules through a *hydrogen bond.* The H may be pictured as leaving its attachment to the Cl and attaching itself to the O, thus forming a hydronium ion, H_3O^+, and leaving the Cl as a chloride ion.

A distinctly polar compound such as NaCl, when dissolved or melted, gives the two kinds of ions each having its own stable octet of electrons. On the other hand, a compound like CH_3Cl cannot undergo so simple a change because the C and Cl are held by a non-polar linkage consisting of a shared electron pair.



$$\mathrm{H}:\overset{\mathrm{H}}{\underset{\mathrm{H}}{\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{C}}}}}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}:$$

If, by any means, the Cl is converted to a chloride ion with a complete octet the remainder would be



$$\left[\mathrm{H}:\overset{\mathrm{H}}{\underset{\mathrm{H}}{\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{C}}}}}\right]^{+}$$

The residue after the removal of the chloride ion would thus have only *six* electrons instead of a stable octet. The production of carbonium ions probably takes place through processes similar to, but surely more complex than, the ionization of HCl with H_2O.

The existence of stabilized carbonium ions is reassuring, but the vast majority of the carbonium ion reactions, as already pointed out, is governed by a transitory existence that forces the carbon to seek another electron pair before it is completely removed from the influence of the former. An electron donor or proton acceptor favourably located in the molecule or about the molecule exerts a 'push' of electrons into the deficiency and thus aids the attacking group in its pull to take away other atoms or groups with their electrons.

The dehydration of an alcohol by an acid will show this.

$$R{-}CH_2{-}CH_2OH + HBr \longrightarrow [RCH_2{-}CH_2OH_2]^+ + Br^-$$

Such oxonium salts as shown above are stable compounds at low temperature, but break down on being heated to give an olefine and water. A bromide ion or more probably an alcohol molecule located in the vicinity of the β-carbon acts as an acceptor of a proton which the molecule needs to expel in order to use the electron pair to supply the deficiency of the adjacent carbon as the molecule of water breaks away.

In spite of the brief half-life of the carbonium ion, it serves as a useful guide to the course of many reactions. Its modes of formation and reactions will be briefly considered. Throughout, the plus sign will indicate a carbon with only six electrons.

I. Formation of Carbonium Ions.

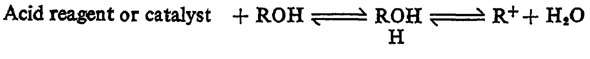
1. *From alkyl halides.* As indicated above, ordinary ionization of such compounds is rare. Even the ionization of trityl halides can be increased by removal of the halogen with its complete octet by means of some reagent such as stannic chloride:

$$(C_6H_5)_3CCl + SnCl_4 \rightleftharpoons SnCl_5^- + (C_6H_5)_3C^+$$

Anhydrous aluminum halides produce similar changes with practically all organic halides.

$$RCl + AlCl_3 \rightleftharpoons AlCl_4^- + R^+$$

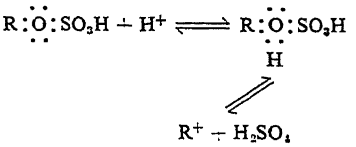
2. *From alcohols by acid reagents or catalysts.* The initial addition of a proton from the reagent forms a relatively stable oxonium compound. Decomposition of this compound by heat or by collision with a suitable reagent gives the carbonium ion.



$$\text{Acid reagent or catalyst} + ROH \rightleftharpoons \underset{H}{ROH} \rightleftharpoons R^+ + H_2O$$

As will be seen later, the reversibility of these changes is of the utmost importance. It cannot be repeated too often that R$^+$ immediately after or even simultaneously for this formation must change to a more stable entity.

Inorganic esters can similarly give carbonium ions. Again, an acid agent or catalyst supplies the protons.

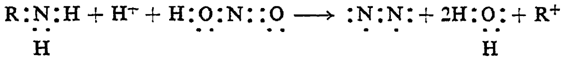


$$R{:}\ddot{\underset{..}{O}}{:}SO_3H + H^+ \rightleftharpoons R{:}\overset{..}{\underset{H}{O}}{:}SO_3H \rightleftharpoons R^+ + H_2SO_4$$

Conversely, carbonium ions formed in the presence of sulphuric acid or its equivalent can reverse the above process. This is very important in polymerizations and alkylations because the esters can act *as reservoirs for carbonium ions.*

Esters are often assumed as intermediates in various processes of these types. It should be noted, however, that any use of a pure neutral ester is naturally ineffective since the ester by itself probably has no more tendency to give ions than does water by itself or hydrogen chloride by itself. On the other hand, the ester in the presence of a suitable donor of protons can form carbonium ions.

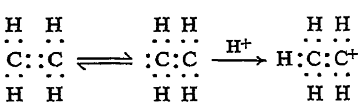
3. *From primary amines by the action of nitrous acid.* This change may be followed in terms of the electrons which appear in the inorganic products:



$$R{:}\underset{H}{\ddot{N}}{:}H + H^+ + H{:}\ddot{\underset{..}{O}}{:}\ddot{N}{:}{:}\ddot{O} \longrightarrow {:}N{:}{:}\!N{:} + 2H{:}\underset{H}{\ddot{O}}{:} + R^+$$

The twenty-six electrons required for the stable products, N_2 and $2H_2O$, leave the alkyl group electronically deficient as a carbonium ion. In this case the latter is formed by a decomposition process which bears no slightest resemblance to any ordinary process of 'ionization'. The varied changes which the carbonium ion can undergo explain the notoriously poor yields of ROH obtainable by the action of nitrous acid upon RNH_2 [13, 1941].

4. Probably the most important formation of a carbonium ion is not by any *separation* process such as those in the above three cases but by *addition to an olefine of a proton* from an acid agent. The addition takes place with the activated or polarized form of the olefine in which the π-electrons have 'moved' away from one member of the unsaturated group.



$$\overset{H\ H}{\underset{H\ H}{C{:}{:}C}} \rightleftharpoons \overset{H\ H}{\underset{H\ H}{{:}C{:}C}} \xrightarrow{H^+} \overset{H\ H}{\underset{H\ H}{H{:}C{:}C^+}}$$

In this case the first product is an ethyl carbonium ion. Its formation could be abbreviated as:

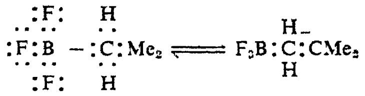
$$CH_2{:}{:}CH_2 + H^+ \rightleftharpoons CH_3CH_2{}^+.$$

In petroleum practices, the most readily formed and most important carbonium ion is that of tertiary butyl:

$$Me_2C{:}{:}CH_2 + H^+ \rightleftharpoons Me_2C^+CH_3.$$

This important carbonium ion will be abbreviated as Me_3C^+ or *t*-Bu$^+$.

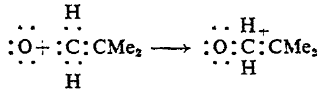
5. *By addition to an olefine of an 'electronically deficient' molecule such as BF_3 or $AlCl_3$.* Such molecules are 'electronically deficient' in that the central atom has only six electrons in the monomeric form. Thus, although they are electrically neutral, they can combine with shifted π-electrons from a double bond. Thus



$$\overset{{:}F{:}}{\underset{{:}F{:}}{{:}F{:}B}} - {:}\overset{H}{\underset{H}{C}}{:}Me_2 \rightleftharpoons F_3B{:}\overset{H_-}{\underset{H}{C}}{:}CMe_2$$

Such a carbonium ion is apparently much more stable than one of the purely hydrocarbon type. The above reaction is apparently much less readily reversed than in the case of the addition of a proton to an olefine. There may be a statistical effect here. Thus the $(CH_3)_3C^+$ can revert to isobutylene by the removal of any one of the *nine* protons without its electron pair. The peculiarities of what might be called the hetero-carbonium ions may be responsible for the complexity of the polymers produced by such reagents as BF_3. It is noteworthy that such a hetero-carbonium ion is a positive ion formed by the union of two neutral molecules, the π-electrons of the olefines having shifted to form a co-ordinate link between C and the hetero atom. This is in contrast to the formation of a positive *t*-butyl carbonium ion by the union of a positive proton from the acid agent with the neutral olefine molecule, the π-electrons of which have shifted to form a true valence link between C and H.

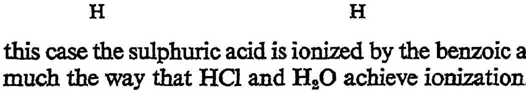
6. *By addition to an olefine of 'atomic oxygen' from an oxidizing agent.*



$${:}\ddot{\underset{..}{O}} + {:}\overset{H}{\underset{H}{C}}{:}CMe_2 \longrightarrow {:}\ddot{\underset{..}{O}}{:}\overset{H_+}{\underset{H}{C}}{:}CMe_2$$

This accounts for the oxidation of olefines to acids having the same number of carbon atoms without the usual splitting of the carbon chain. In this case the final oxidation product of isobutylene is isobutyric acid instead of acetone. The carbonium ion formed by the addition of the O 'atom' with its sextet of electrons undergoes a shift of an electron pair with its proton to give isobutyraldehyde.

7. *By addition to a carbonyl group of a proton from a suitable agent.* This reaction is of the greatest importance in general organic reactions. A good example is Hammett's discovery of the cryoscopic behaviour of benzoic acid in 100% sulphuric acid in which the freezing-point depression is twice that calculated from the amount of benzoic acid added.



$$C_6H_5{:}\underset{\underset{H}{{:}\ddot{O}{:}}}{C}{:}{:}O + H_2SO_4 \longrightarrow C_6H_5{:}\underset{\underset{H}{{:}\ddot{O}{:}}}{C_+}{:}\ddot{O}{:}H + HSO_4^-$$

In this case the sulphuric acid is ionized by the benzoic acid in much the way that HCl and H_2O achieve ionization.

II. Reactions of Carbonium Ions.

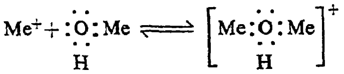
As might be expected from its electronically deficient structure, the reactions of this ion are not like those of ordinary ions which are dependent usually on the rate of addition of a reagent. Simultaneously with the formation of a carbonium ion or immediately thereafter it must undergo a change. If the carbonium ion cannot satisfy its electronic deficiency *intermolecularly*, it must change *intramolecularly* and a *rearrangement* occurs.

It should be noted that the order of stability of these very unstable fragments is as follows:

tertiary >> secondary > primary.

This order corresponds to the rapidity of formation of RCl from the three classes of alcohols.

1. It might appear that the easiest change for a carbonium ion would be its *union with an ion or molecule with a complete octet of electrons but having at least one free pair.* Thus, a methyl carbonium ion formed in aqueous methanol by the action of nitrous acids with methylamine is immediately stabilized by union with one of the free pairs of electrons of the solvent.



$$\mathrm{Me^{+} + :\underset{H}{\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}}:Me \rightleftharpoons \left[Me:\underset{H}{\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}}:Me\right]^{+}}$$

The product is the more stable oxonium ion. This can give a proton to the medium and thus become dimethyl ether, the chief product of the reaction.

If the action of methylamine with nitrous acid is carried out in aqueous solution, the products include methanol and dimethyl ether, the former being the result of co-ordination of the methyl carbonium ion with water, followed by loss of a proton to the medium. This conception of the co-ordination of the carbonium ion with the medium is much more plausible than the ordinary idea that the carbonium ion unites with hydroxyl ions from the water or methoxyl ions from methanol.

The reversible addition of R^+ to sulphuric acid to give an ester as mentioned above is another important intramolecular stabilization of the carbonium ion.

The carbonium ion can also unite with ordinary anions. This is well illustrated in the action of *n*-butylamine with nitrous acid during which the Bu^+ ion forms not only BuOH but also BuCl and BuONO with the chloride and nitrite ions in the solution. The larger amount of the first product is not due to any action of hydroxyl ions but to the co-ordination of the carbonium ion with the water.

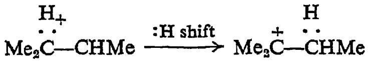
In many cases the carbonium ion stabilizes itself *intramolecularly. The electronically deficient carbon atom takes an electron pair from an adjacent atom.* The mechanism of this apparently simple transfer of an electron pair from one atom to the adjacent atom is now being attacked by mathematical physical chemists. Depending on the structure of the molecule, this transfer of an electron pair may take place *either with or without the proton or the group attached to the moving electron pair* [14, 1932].

2. The needed electron pair may come *from an adjacent multiple linkage*, giving an *allylic shift*. This change is not important in most processes, but will be considered briefly because the usual peculiarities of the carbonium ion appear. The replacement by bromine of hydroxyl in crotyl alcohol is a good example. The OH is removed in the usual way, probably through an oxonium compound. The resulting crotyl carbonium ion then undergoes the simplest possible internal shift of an electron pair.

$$\mathrm{MeCH::CH:\overset{+}{C}H_2 \xrightarrow{:shift} Me\overset{+}{C}H:CH::CH_2}$$

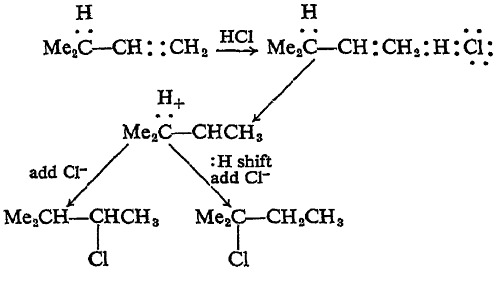
Only the essential electrons are indicated. As usual, the change is reversible. The product is formed by the union of these two carbonium ions with bromide ions to give a mixture of crotyl bromide and methylvinylbromomethane.

3. *The electron pair may take with it an attached proton.* A good example of this type of change is the replacement by Cl of OH in 2-methyl-3-butanol. All reagents which bring about this change give only the 2-chloro compound instead of the 3-chloro compound. As usual, the first change is undoubtedly the formation of an oxonium compound from the alcohol. This then gives the corresponding secondary carbonium ion. The shift of an electron pair with its attached proton converts the secondary carbonium ion to the more stable tertiary one which then combines with the chloride ion to give the observed product.



$$\mathrm{Me_2\overset{H_+}{\overset{\cdot\cdot}{C}}{-}CHMe \xrightarrow{:H\ shift} Me_2\overset{+}{C}{-}\overset{H}{\overset{\cdot\cdot}{C}}HMe}$$

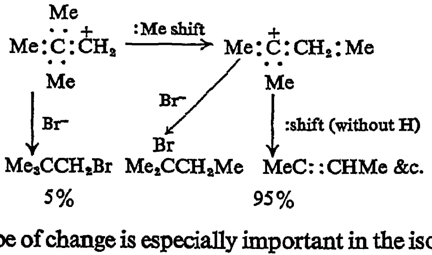
Only the electrons involved in the shift are indicated. The desired 2-methyl-3-chlorobutane can be obtained in 50% yield by adding dry HCl to isopropylethylene in the cold [15, 1933]. Even under these conditions, an equal amount of the rearranged 2-chloro compound is obtained. It is important to note that the latter is not formed by rearrangement of the 3-chloro compound which is found to be completely stable under the conditions used. The steps involved in the formation of the two products are instructive.



The initial attack of the dry hydrogen chloride on the dry olefine may take place through a hydrogen bond involving the shifted π-electrons of the double linkage. It would thus resemble the mechanism of the ionization of HCl in water.

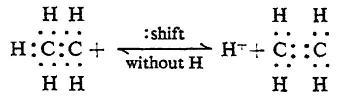
4. The moving electron pair may *carry an attached organic group with it* to give ordinary 1,2-rearrangement. In general, the rearrangement of an electron pair with the attached organic group (:R) takes place more readily than does that of :H. Usually the larger the group, the more readily it rearranges.

Perhaps the most notorious example of 1,2-rearrangement is the action of neopentyl alcohol with HBr to give rearrangement products and only 5% of neopentyl bromide [16, 1932]. In this case the alcohol absorbs almost exactly 1·0 mol of HBr in the cold. This HBr can be removed by a stream of inert gas or by washing with water to leave the original alcohol with practically unchanged freezing-point (50°). On the other hand, heating the oxonium compound in a sealed tube or letting it stand a long time gives mainly *t*-amyl bromide, isoamylenes, and 5% neopentyl bromide. The relatively stable oxonium compound decomposes to give water and the neopentyl carbonium ion. Only 5% of these ions stabilize themselves by union with the bromide ions without rearrangement.



This type of change is especially important in the isomerization and polymerization of olefines and in alkylation. Examples to be considered later include (*a*) the acid catalysed dehydration of isobutyl alcohol to a 1 : 1 : 1 mixture of 1- and 2-butenes and isobutylene, and (*b*) the isomerization of olefines such as tetramethylethylene.

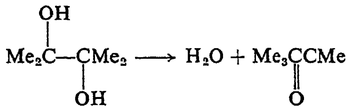
5. The electron pair may move to the electronically deficient carbon *without taking its attached proton.* The result is a multiple linkage. The dehydration of ethanol to ethylene is an example. The ethyl carbonium ion is formed at high temperature from an oxonium compound or an ester such as a sulphate or a phosphate.



$$\mathrm{H{:}\overset{H}{\underset{H}{C}}{:}\overset{H}{\underset{H}{C}}+ \xrightarrow[\text{without H}]{:\text{shift}} H^{+}+\overset{H}{\underset{H}{C}}{::}\overset{H}{\underset{H}{C}}}$$

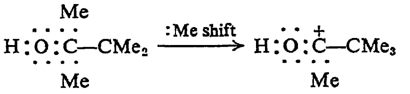
This change is often referred to as the *expulsion of a proton* from the carbonium ion. More probably, the proton is taken by the medium or the catalyst or by another molecule of alcohol or ester at the same time that the electron pair moves. Most of the changes considered here have this twofold character of 'push and pull'. These changes, along with the removal of water from the oxonium compound or the proton attack on the ester, are merely phases of an instantaneous readjustment into a new pattern of the atoms in the molecule.

The classical rearrangement, that of pinacol to pinacolone, involves the last two types of changes discussed.



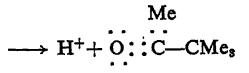
$$\mathrm{Me_2\overset{OH}{C}—\underset{OH}{C}Me_2 \longrightarrow H_2O + Me_3C\underset{O}{\overset{\|}{C}}Me}$$

The acid dehydrating agent first attacks one of the OH groups and the resulting oxonium compound decomposes in the usual way to give a carbonium ion in which the electronically deficient carbon stabilizes itself by attracting from the adjacent atom an electron pair with the attached methyl group.



$$\mathrm{H{:}O{:}\overset{Me}{\underset{Me}{C}}—CMe_2 \xrightarrow{:\text{Me shift}} H{:}O{:}\overset{+}{\underset{Me}{C}}—CMe_3}$$

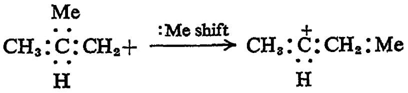
This peculiar carbonium ion is unusually easy to stabilize because the only requirement is that the pair of electrons holding the proton to the oxygen shift towards the electronically deficient carbon, thus creating a carbonyl group.



$$\mathrm{\longrightarrow H^{+}+ O{::}\overset{Me}{C}—CMe_3}$$

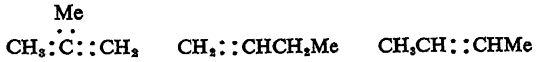
Again, the proton is probably absorbed by the medium, the catalyst or another molecule of the glycol, rather than merely being expelled by the carbonium ion.

Similar changes occur in the dehydration of isobutyl alcohol by acid catalysts.



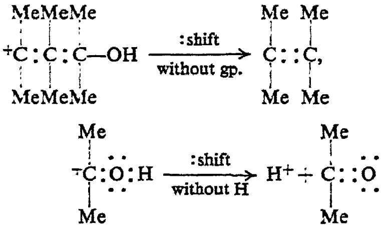
$$\mathrm{CH_3{:}\overset{Me}{\underset{H}{C}}{:}CH_2+ \xrightarrow{:\text{Me shift}} CH_3{:}\overset{+}{\underset{H}{C}}{:}CH_2{:}Me}$$

The satisfaction of the electronically deficient C by shift of an adjacent pair without its proton gives the observed butylenes.



$$\mathrm{CH_3{:}\overset{Me}{C}{::}CH_2 \qquad CH_2{::}CHCH_2Me \qquad CH_3CH{::}CHMe}$$

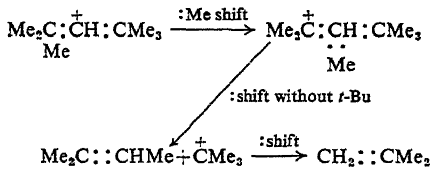
6. The electron pair may move *without the attached group* if the latter is tertiary. An old example of this change is the reaction of Me_6-trimethylene glycol with even a trace of an acid reagent to give acetone and Me_4-ethylene. The oxonium compound is apparently formed very readily but immediately decomposes. The resulting carbonium ion stabilizes itself by attracting an electron pair from the adjacent carbon without the large tertiary structure held by it. For emphasis and clarity only two electron pairs are indicated in the carbonium ion.



$$\mathrm{{}^{+}\overset{Me}{\underset{Me}{C}}{:}\overset{Me}{\underset{Me}{C}}{:}\overset{Me}{\underset{Me}{C}}—OH \xrightarrow[\text{without gp.}]{:\text{shift}} \overset{Me}{\underset{Me}{C}}{::}\overset{Me}{\underset{Me}{C}},}$$

$$\mathrm{{}^{+}\overset{Me}{\underset{Me}{C}}{:}O{:}H \xrightarrow[\text{without H}]{:\text{shift}} H^{+}+\overset{Me}{\underset{Me}{C}}{::}O}$$

The important new type of change here illustrated is the movement of the electron pair away from the tertiary group to the electronically deficient carbon. This type of change is involved in the fission (not cracking) of higher-branched olefines. The following steps are probably involved.



$$\mathrm{\underset{Me}{Me_2C}{:}\overset{+}{C}H{:}CMe_3 \xrightarrow{:\text{Me shift}} Me_2\overset{+}{C}{:}\underset{Me}{CH}{:}CMe_3}$$

$$\xrightarrow{:\text{shift without } t\text{-Bu}} \mathrm{Me_2C{::}CHMe+\overset{+}{C}Me_3 \xrightarrow{:\text{shift}} CH_2{::}CMe_2}$$

By similar changes, the polyisobutylenes can be depolymerized to isobutylene. Good examples of the inadvertent occurrence of such depolymerization reactions are given by the condensation of phenol with diisobutylene and with triisobutylene. In the presence of sulphuric acid, the first readily gives phenol substituted in the para-position by the $—CMe_2CH_2CMe_3$ group. All attempts to obtain a phenol substituted by a 'triisobutyl' group have failed, the result being a mixture of the product just mentioned and *t*-butylphenol. In other words, sulphuric acid strong enough to induce reaction with the larger and more sluggish triisobutylene is strong enough to split off a *t*-$\mathrm{Bu^{+}}$ in exactly the same way as occurred in the last set of equations. This reacts with the phenol. The remaining diisobutylene reacts with another phenol.

Fissions like those outlined above, resulting from the shift of an electron pair *without* its attached tertiary group, give the clue to the mechanism of acid-catalysed polymerization of olefines.

In recapitulation, it should be emphasized that all of the above changes of the carbonium ion are merely different ways of converting an unstable *open sextet of electrons* to a *stable octet.* One important additional way of achieving this same end appears under very special conditions.

7. A carbonium ion may take an electron pair and its attached proton *from another molecule* if the structure of the latter and the conditions are suitable. (The conditions are those for 'alkylation'.) Since the order of decreasing stability of alkyl carbonium ions is tertiary to secondary to primary, a tertiary hydrocarbon such as isobutane or isopentane should most readily part with an electron pair and its attached proton.

$$\mathrm{Me{:}\overset{Me}{\underset{Me}{C}}{:}H}$$

The conditions must be such as to prevent other changes and favour this one. The net result is an important new type of reaction.

$$R^+ + Me_3C{:}H \longrightarrow RH + Me_3C^+$$

III. Alkylation.

As carried out with an olefine and a very large excess of a tertiary hydrocarbon in the presence of concentrated sulphuric acid or other equivalent catalyst, this process involves the following steps which have already been described:

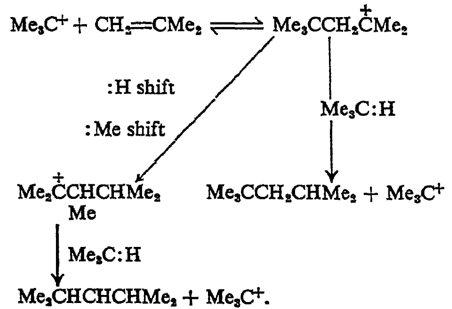
1. Addition of a proton to the olefine.
2. Reversible union with the sulphuric acid of the carbonium ion thus formed.
3. Addition to the olefine of the small R^+ as the latter is formed or, more probably, as obtained from the 'reservoir' formed in 2. The result is a larger carbonium ion, R'^+.
4. Reaction of the larger carbonium ion with $Me_3C{:}H$ or other tertiary hydrocarbon to give R'H, a final alkylation product, and Me_3C^+ or other tertiary carbonium ion which starts the chain again.
5. At all stages, the carbonium ions can undergo the usual rearrangements.
6. The loss of a proton by a carbonium ion to give the corresponding olefine is apparently repressed by the concentrated sulphuric acid which combines with the carbonium ion until such time as one of the large number of tertiary hydrocarbon molecules enters the reaction.

These principles may be illustrated by the action of isobutylene with a large excess of isobutane in the presence of concentrated sulphuric acid.

$$Me_2C{=}CH_2 + H^+ \rightleftharpoons Me_3C^+,$$

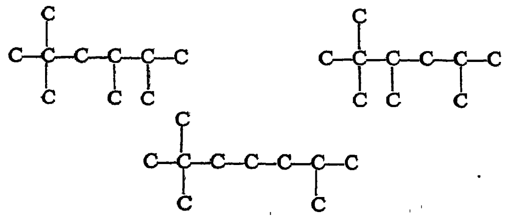
$$Me_3C^+ + H_2SO_4 \rightleftharpoons Me_3COSO_3H + H^+$$

(Reservoir)



These octanes are two of the chief alkylation products. Other products are formed in smaller amounts and presumably by more steps.

The alkylation of 1,1-methylisopropylethylene with an excess of isobutane gives a decane fraction, about one-third of which comprises the following structures in decreasing amounts:



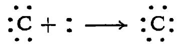
The first of these represents the addition of t-Bu$^+$ to the olefine to give a C_{10} carbonium ion which reacts with the excess of isobutane to give the observed product and t-Bu$^+$ to start the chain over again.

The next involves the conversion of the olefine to Me_3CCHCH_3 by the usual changes. The addition of this carbonium ion to isobutylene formed from t-Bu$^+$ would give the C_{10} carbonium ion of the second structure.

The last might be formed by addition of an isobutyl carbonium ion to t-bu-ethylene. The formation of the isobutyl carbonium ion is unusual, to say the least. There are many other combinations of simple steps which would give the observed product. Unfortunately there is still too little definite information on the fundamentals which control the possible steps.

A comforting circumstance which recurs repeatedly in complicated hydrocarbon chemistry is illustrated by the above three decanes. Usually the products found in largest amounts are those which involve the simplest and least numerous of the changes possible to carbonium ions.

It should again be emphasized that all the reactions of the carbonium ion, even this last and very remarkable one, involve the same fundamental change, namely,



$$:\overset{\cdot\cdot}{\underset{\cdot\cdot}{C}} + : \longrightarrow :\overset{\cdot\cdot}{\underset{\cdot\cdot}{C}}:$$

Carbanion or Basic Reactions

When studies of the reaction order and rate indicate a dependence on basic or negative ion concentration, the main driving force of an organic reaction may be assigned to the presence of atoms carrying unshared electrons. Such reactions are called 'basic reactions' as a general term, and in those cases where it applies, the more specific term 'carbanion reactions' is used.

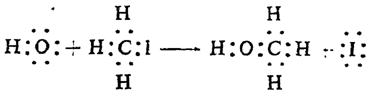
Because of complexities that are introduced by the basic character of oxygen, sulphur, nitrogen, and similar elements when they are present in organic molecules, it is necessary to take a more general view of negative ion reactions than of the positive ion reactions.

In carbonium ion reactions, the deficiency of positive character is usually localized on a carbon atom. Correspondingly in a great many basic reactions the unshared electrons create a negative centre by localizing on a carbon atom. This presents a situation comparable, but opposite in character, to that of carbonium ion formation. Such is the case when a basic attack results in the substitution of one negative group for another, or the extraction of any group from carbon without the bonding electrons. It is also true when a compound such as R:Y ionizes to give $R{:}^- \; Y^+$ or when a negative group adds to a carbon-carbon double bond displacing the π-electrons towards the other carbon. In all these reactions unshared electrons are to some extent localized on a carbon atom, thereby creating a basic reaction intermediate usually designated as a carbanion.

However, when a simple or molecular ion with unshared electron reacts with an organic molecule containing such atoms as oxygen, nitrogen, and sulphur, the attack is often on carbon, leaving the negative charge and unshared electrons located on the oxygen, nitrogen, or similar atom. Such reaction intermediates are not carbanions (by definition) but electronically they behave in a similar manner and can be treated in much the same way as carbanion reactions.

Negative reagents, including carbanions, generally react with organic compounds by substitution, addition, and elimination, and often lead to a combination of steps involving all three.

The simplest substitution reaction is the direct displacement of one group attached to carbon by another group which carries an unshared electron pair [6, 1938].



$$\mathrm{H}:\ddot{\underset{..}{\mathrm{O}}}: + \mathrm{H}:\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}:\mathrm{I} \longrightarrow \mathrm{H}:\mathrm{O}:\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}:\mathrm{H} + :\ddot{\underset{..}{\mathrm{I}}}:$$

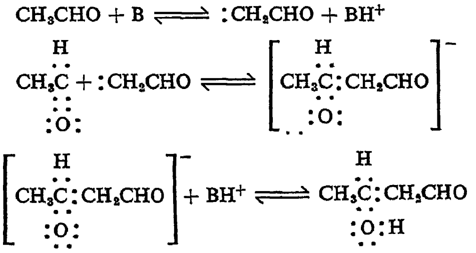
Reaction-rate studies leave little doubt that reactions of this type follow the course of simultaneous formation of new and rupture of old bonds, and that the driving force is the affinity of the oxygen electrons for carbon. The mode of attack by the hydroxyl group has been explained from stereochemical consideration to be a back side approach opposite the apex of the tetrahedron formed by the group that is being displaced. As the hydroxyl group approaches the centre of the face opposite the vertex occupied by the iodine, the carbon-iodine bond weakens and stretches to a point of final release as the new bond forms between the carbon and oxygen. The complete retention and inversion of optical activity in such reactions leaves little doubt as to the validity of the above mechanism.

Other reactions which proceed by the nucleophylic displacement on carbon are the Williamson ether synthesis in which $:\ddot{\underset{..}{\mathrm{O}}}:\mathrm{R}$ displaces a halogen from RX, and the alkylation of acetoacetic and malonic esters in which the carbanion of the ester, R: (formed through loss of an acidic hydrogen), displaces a halogen from $\mathrm{R}:\ddot{\underset{..}{\mathrm{X}}}:$ to give $\mathrm{R}:\mathrm{R} + :\ddot{\underset{..}{\mathrm{X}}}:$.

To obtain the carbanion used in the displacement reactions of acetoacetic ester alkylations and other similar reactions, it is necessary for the carbonyl compound to lose a proton—thus generating $\mathrm{R}:^-$ and H^+.

Just as an OH group can approach the back side of a tetravalent carbon and establish a bond to that carbon with a resultant loss of the vertex substituent, an OH group can also approach a hydrogen and establish a new bond due to the affinity of oxygen electrons for hydrogen (particularly an acidic one as in acetoacetic ester). Rupture of the old bond with simultaneous establishment of the new gives $\mathrm{H}:\ddot{\underset{..}{\mathrm{O}}}:\mathrm{H}$ and R:—the carbanion—by displacement.

Besides reacting by nucleophylic substitutions as shown in the alkylation of acetoacetic ester, carbanions also react by addition as in the aldol condensation:



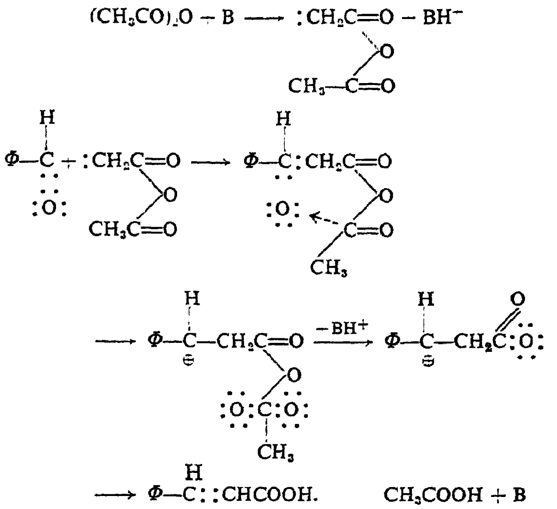
$$\mathrm{CH_3CHO} + \mathrm{B} \rightleftharpoons :\mathrm{CH_2CHO} + \mathrm{BH^+}$$

$$\mathrm{CH_3}\overset{\mathrm{H}}{\underset{:\ddot{\mathrm{O}}:}{\ddot{\mathrm{C}}}} + :\mathrm{CH_2CHO} \rightleftharpoons \left[\mathrm{CH_3}\overset{\mathrm{H}}{\underset{:\ddot{\mathrm{O}}:}{\mathrm{C}}}:\mathrm{CH_2CHO}\right]^-$$

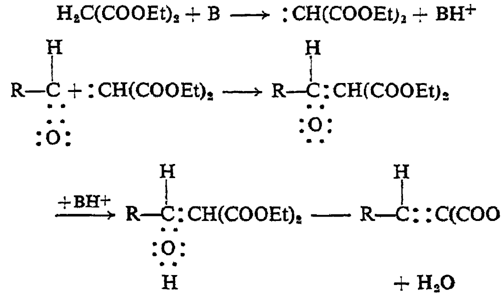
$$\left[\mathrm{CH_3}\overset{\mathrm{H}}{\underset{:\ddot{\mathrm{O}}:}{\mathrm{C}}}:\mathrm{CH_2CHO}\right]^- + \mathrm{BH^+} \rightleftharpoons \mathrm{CH_3}\overset{\mathrm{H}}{\underset{:\ddot{\mathrm{O}}:\mathrm{H}}{\mathrm{C}}}:\mathrm{CH_2CHO}$$

Thus the carbanion formed by a displacement attacks the positive carbon of an aldehyde molecule, creating a conjugate base which stabilizes itself by taking a proton.

A large number of base-catalysed reactions undoubtedly proceed through a carbanion mechanism similar to the acetoacetic ester and aldol condensation. In the Perkins reactions the base, such as alkali acetate, carbonate or pyridine, extracts a proton from the anhydride to give a carbanion. The mechanism might be as follows:



Compounds containing methylene or acidic hydrogens react with aldehydes in the presence of secondary amines (Knowlenagel) by the same mechanism.

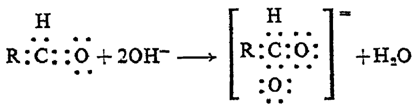


$$\mathrm{H_2C(COOEt)_2} + \mathrm{B} \longrightarrow :\overline{\mathrm{CH(COOEt)_2}} + \mathrm{BH^+}$$

$$\mathrm{R}\text{—}\overset{\mathrm{H}}{\underset{:\ddot{\mathrm{O}}:}{\mathrm{C}}} + :\mathrm{CH(COOEt)_2} \longrightarrow \mathrm{R}\text{—}\overset{\mathrm{H}}{\underset{:\ddot{\mathrm{O}}:}{\mathrm{C}}}:\mathrm{CH(COOEt)_2}$$

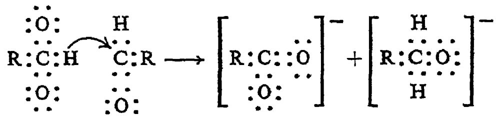
$$\xrightarrow{+\mathrm{BH^+}} \mathrm{R}\text{—}\overset{\mathrm{H}}{\underset{\underset{\mathrm{H}}{:\ddot{\mathrm{O}}:}}{\mathrm{C}}}:\mathrm{CH(COOEt)_2} \longrightarrow \mathrm{R}\text{—}\overset{\mathrm{H}}{\mathrm{C}}::\mathrm{C(COOEt)_2} + \mathrm{H_2O}$$

Aldehydes such as benzaldehyde and formaldehyde which contain no α-hydrogens cannot undergo the typically basic aldol condensation and resort to a complicated fourth-order reaction known as the Cannizzaro reaction. The first step of this reaction



$$\mathrm{R}:\overset{\mathrm{H}}{\mathrm{C}}::\ddot{\mathrm{O}} + 2\mathrm{OH^-} \longrightarrow \left[\mathrm{R}:\overset{\mathrm{H}}{\underset{:\ddot{\mathrm{O}}:}{\mathrm{C}}}:\ddot{\mathrm{O}}:\right]^{=} + \mathrm{H_2O}$$

probably forms an intermediate in which the high electron density on the two oxygens produces a highly acidic hydrogen and causes a transfer of the hydrogen with its bonding electrons to the carbon of another aldehyde molecule [3*d*, 1940]. The result is an inter-molecular rearrangement.

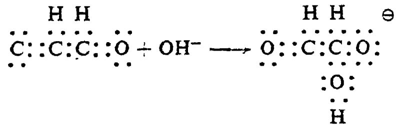


$$\mathrm{R}:\overset{:\ddot{\mathrm{O}}:}{\underset{:\ddot{\mathrm{O}}:}{\mathrm{C}}}:\mathrm{H} \quad \overset{\mathrm{H}}{\underset{:\ddot{\mathrm{O}}:}{\mathrm{C}}}:\mathrm{R} \longrightarrow \left[\mathrm{R}:\underset{:\ddot{\mathrm{O}}:}{\mathrm{C}}::\mathrm{O}\right]^- + \left[\mathrm{R}:\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}:\ddot{\mathrm{O}}:\right]^-$$

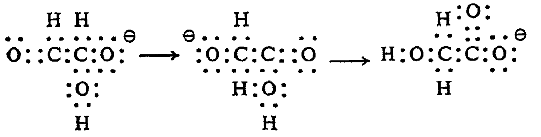
Instead of generating a carbanion, the basic attack has produced a hydride ion, which attacks the positive carbon of the carbonyl component just as the carbanion does in the aldol condensation. Electronically, the reactions are the same at this step, but lead to entirely different products.

In general, the basic attack leads to a nucleophylic reagent. This reagent, R:, subject to its environment, will take the easiest way available to share its electrons.

Glyoxal, under the conditions of the aldol condensation, undergoes an internal Cannizzaro because it is the easiest way out [3*d*, 1940]. The basic attack, in the absence of an α-hydrogen, gives



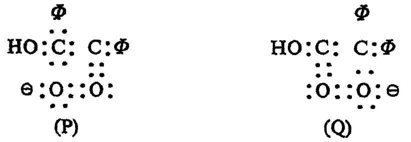
The attack of the second hydroxyl is not necessary in this case because the intramolecular rearrangement of the hydrogen is much easier than the intermolecular rearrangement in benzaldehyde and formaldehyde.



Thus the strong push from the negative centre and the weak pull from the positive carbonyl combine to bring about the rearrangement of the H: and the production of a molecule stable to the basic environment.

If the hydrogens of glyoxal are replaced with phenyl groups, the compound is benzil and the reaction is the benzilic rearrangement. Thus the aldol condensation, the Cannizzaro reaction, the internal Cannizzaro reaction of glyoxal, and the benzilic acid rearrangement as well as many other reactions are ionically very similar, but due to variances in molecular structure are superficially different. In the basic reactions, as in the acidic reaction, it cannot be emphasized too strongly that the opposite effect must not be forgotten. The push cannot happen unless there is some pull. Unless there were some tendency for the electrons of $R_2C::O$ to localize on the oxygen, the nucleophylic attack of R: would never go to completion.

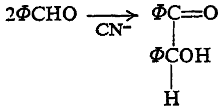
The importance of this double effect has already been shown, but derives emphasis from a further discussion of the benzilic acid rearrangement. Most rearrangements of this type stem from carbonium ions. Efforts to explain this rearrangement as such have failed. And even though the reaction is base catalysed, a complete explanation cannot neglect the electron-deficient carbon. An explanation of the mechanism of this reaction lies in an understanding of both effects, as has been excellently stated by Hammett [3*e*, 1940]:

> 'This reaction exhibits a specific hydroxyl ion catalysis . . . and is proportional to the concentration of the ion (P) formed by the reversible addition of hydroxyl ion to one carbonyl group. The reaction can therefore be accounted for by the shift of a *phenyl group with its bonding pair*
>
> 
>
>
> The addition of a proton to (Q) yields benzilic acid. The reaction is, in essence, similar to the Wagner-Meerwein rearrangement, the carbon atom of the carbonyl group in (P) carries only six electrons in one of the resonating structures, and the rearrangement consists in the shift to this carbon from the adjacent carbon of a phenyl group along with its bonding pair.'

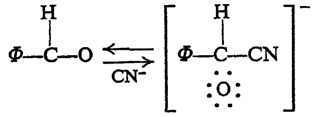
Although the carbonyl carbon is only weakly electrophylic, it is nevertheless this weak deficiency that makes it possible for the phenyl group with its electrons to rearrange. However, as Hammett also explains, the rearrangement is due more to the negative push on the phenyl than to the positive pull from the carbonyl carbon.

The benzoin condensation is another good example of how an activated molecule prohibited by molecular structure from taking a normal reaction course will, if possible, satisfy itself by taking another peculiarly different course. *Electronically, however, the reaction is the same.*

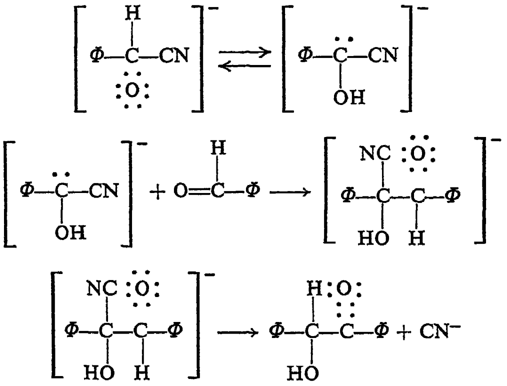
Benzaldehyde is specifically catalysed by cyanide to give benzoin:



The normal extraction of an α-hydrogen to give a carbanion cannot take place. Therefore, this aldol-type product must have been formed through some effect of the cyanide ion.

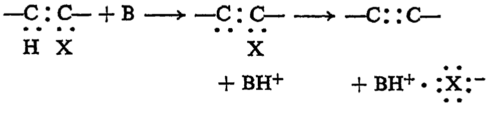


Through the *specific effects of the attached cyanide ion*, the benzaldehyde is now capable of undergoing a condensation similar to the normal aldol condensation.

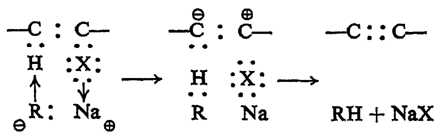


For many other basic reactions similar mechanisms can be written. The Grignard reaction is definitely a basic addition reaction, which resembles those involving carbonyl compounds that have been previously discussed. The complexities of the reaction, however, are so great that no general agreement has been reached on the exact mechanism of this most versatile reaction.

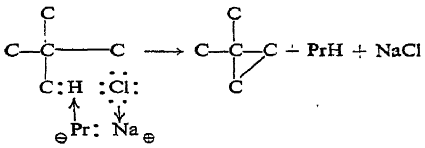
Basic elimination reactions such as dehydrohalogenation probably proceed through the formation of a carbanion [4, 1940].



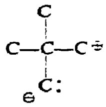
A better representation of the actual mechanism is probably



Neopentyl chloride treated with propylsodium cannot form an olefine so reacts as follows [17, 1942]:



With no α-hydrogens available an unactivated β-hydrogen is attacked by the propyl carbanion and removed as a proton, followed by a release or extraction of the chloride ion to give



The two methyl groups on the neocarbon probably aid the molecule in establishing a cyclopropane ring by pushing the positive and negative carbons closer together.

REFERENCES

1. Branch, G. E. K., and Calvin, Melvin. *The Theory of Organic Chemistry* (Prentice Hall, 1941), p. 27.
2. Brown, H. C., Kharasch, M. S., and Chao, T. H. *J. Am. Chem. Soc.* **62**, 3435 (1940).
3. Hammett, Louis P. *Physical Organic Chemistry* (McGraw Hill Book Co., 1940): (*a*), p. 368; (*b*) p. 380; (*c*) p. 54; (*d*) p. 351; (*e*) p. 321.
4. Hauser, C. R. *J. Am. Chem. Soc.* **62**, 933 (1940).
5. Horn, E., Polanyi, M., and Style, D. W. G. *Zt. Physik. Chem.* **B23**, 291 (1933).
6. Hughes, E. D. 'Aliphatic Substitution and the Walden Inversion', *Trans. Faraday Soc.*, No. 201, **34**, part 1 (1938).
7. Kharasch, M. S., Kane, S. S., and Brown, H. C. *J. Am. Chem. Soc.* **64**, 1621 (1942).
8. Kharasch, M. S., Mansfield, J. V., and Mayo, F. R. *J. Am. Chem. Soc.* **59**, 1155 (1937).
9. Lewis, G. N. *The Valence and Structure of Atoms and Molecules* (Chem. Cat. Co., 1923).
10. Paneth, F., and Hofeditz, W. *Ber. d. deutschen Chem. Ges.* **62**, 1335 (1929).
11. Price, Charles C. *Mechanisms of Reactions at Carbon-Carbon Double Bonds* (Interscience Publishers, 1946): (*a*) pp. 2 and 3; (*b*) pp. 70–91; (*c*) p. 77.
12. Rice, F. O., and Teller, Edward. *The Structure of Matter* (John Wiley & Sons, Inc., 1949), p. 2.
13. Whitmore, F. C., and Thorpe, R. S. *J. Am. Chem. Soc.* **63**, 1118 (1941).
14. Whitmore, F. C. *J. Am. Chem. Soc.* **54**, 3274 (1932).
15. Whitmore, F. C., and Johnston, F. *J. Am. Chem. Soc.* **55**, 5020 (1933).
16. Whitmore, F. C., and Rothrock, H. S. *J. Am. Chem. Soc.* **54**, 3431 (1932).
17. Whitmore, F. C., and Zook, H. D. *J. Am. Chem. Soc.* **64**, 1783 (1942).
18. Ziegler, K. *Ann. Rept. Chem. Soc.* (London), 1928, 156.

THE FRACTIONATION, ANALYSIS, AND ISOLATION OF HYDROCARBONS IN PETROLEUM

By BEVERIDGE J. MAIR and FREDERICK D. ROSSINI
National Bureau of Standards, Washington, D.C.

I. Introduction

A COMPREHENSIVE investigation on the isolation and identification of hydrocarbons in petroleum was begun in 1927 at the National Bureau of Standards under the direction of Edward W. Washburn [57, 82].[1] This work, sponsored jointly by the American Petroleum Institute and the National Bureau of Standards, and carried on as the A.P.I. Research Project 6, has to date involved a total of about 200 man-years of research and has resulted in the separation of seventy-two hydrocarbons from one crude petroleum with a number of additional compounds nearing completion. This report summarizes the results obtained to date by this project on the gas, gasoline, kerosine, and lubricant fractions of one intermediate crude petroleum and on the gasoline fraction of seven representative crude petroleums.

II. General Method of Operation

Substantially all of the hydrocarbons in petroleum are composed of paraffin groups, cycloparaffin or naphthene groups, aromatic groups, mixed aromatic-naphthene nuclei, or combinations of these. No olefine or acetylene hydrocarbons appear to be in naturally occurring petroleum in any significant amount.

The problem is that of separating, without altering the constituents, the complex mixture of hydrocarbons that constitute petroleum, and to obtain the major components in a substantially pure state. The general method of operation is to utilize the various processes of fractionation in such combinations as will produce a 'sifting' of the molecules with respect to size on the one hand and to type on the other.

III. Processes of Fractionation

To be successful in separating a given mixture of hydrocarbons, any process of fractionation must be one that involves a physical property that has significantly different values for the several components of the mixture to be separated. Furthermore, the procedure must be one for which there is available, or can be developed, a workable apparatus.

The standard processes of fractionation used in this work are those of distillation, extraction, adsorption, and crystallization, which involve the properties of vapour pressure (or boiling-point), solubility, adsorbability, and freezing-point (and cryoscopic constant).

These processes of fractionation may be used in several variations, as follows:

Distillation: (*a*) at different pressures; (*b*) with an added volatile azeotrope-forming substance (for azeotropic distillation); (*c*) with an added relatively non-volatile selective solvent (for extractive distillation).

Extraction: (*a*) at different temperatures; (*b*) with different single solvents (with two liquid phases); (*c*) with different multiple solvents (with three liquid phases).

Adsorption: (*a*) at different temperatures; (*b*) with different adsorbents; (*c*) with the hydrocarbons in the gas phase; (*d*) with the hydrocarbons in the liquid phase; (*e*) with diluting liquids; (*f*) with desorbing liquids.

Crystallization: (*a*) from the mixture of hydrocarbons alone; (*b*) from a solution of the hydrocarbons in an appropriate solvent; (*c*) with centrifuging.

With regard to the nature of the separation obtained, the foregoing processes of fractionation, excluding crystallization, may be classified according to whether they fractionate primarily with respect to size of molecule or to type of molecule. Separation primarily according to size of molecule (or boiling-point or molecular weight) is produced by distillation at one fixed pressure. Separation primarily according to type of molecule is produced by distillation alternately at two fixed pressures, by azeotropic distillation, by extractive distillation, by extraction, and by adsorption. In connexion with separations by type it is important to note (see later) that, except in certain special cases, alternate distillation at two fixed pressures, distillation with an azeotrope-forming substance, and extractive distillation, require a charging-stock that is homogeneous with respect to boiling-point (or size of molecules), that is, a relatively narrow-boiling charge. On the other hand, the process of extraction may be used successfully on rather wide-boiling charges, and the process of adsorption may be used on extremely wide-boiling material.

In connexion with separation by crystallization, two general statements may be made regarding hydrocarbons: (*a*) for a given degree of symmetry of the molecule the freezing-point usually is higher the greater the size of the molecule, (*b*) for a given number of carbon atoms in the molecule, the freezing-point usually is higher the greater the symmetry of the molecule.

Except for those few hydrocarbons in the volatile range that have boiling-points relatively far from their neighbours and except for certain other hydrocarbons present in relatively large amount (as normal paraffins in a Pennsylvania or a Mid-Continent petroleum), regular distillation alone will not separate pure hydrocarbons from petroleum, and one or more of the other methods (including the variations of distillation) must also be used.

The order in which the several methods are used is determined by the effectiveness of a given process in increasing the separation attained by the preceding method. Thus, although a given process may be ineffective when used alone, its systematic use in appropriate combination with other processes can often lead to the complete separation of an otherwise unseparable constituent.

IV. Distillation

Distillation is the most important fractionating process for separating hydrocarbons of the gas, gasoline, and kero-

---

[1] The numbers in brackets refer to the publications of the A.P.I. Research Project 6 listed at the end of this paper.

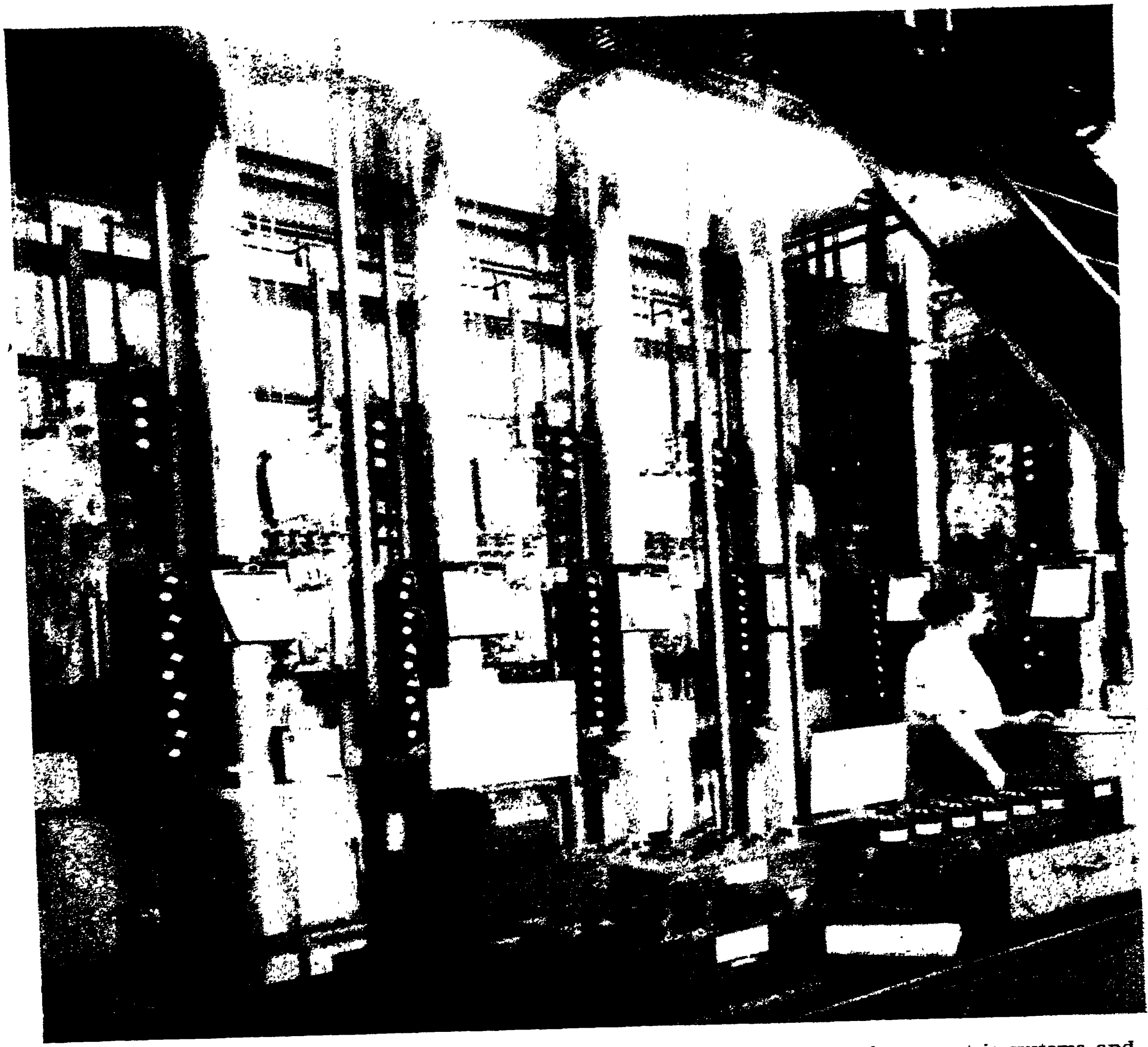


FIG. 1. View in the distillation laboratory, showing the instruments for the thermometric systems and the lower part of columns 5 to 10, inclusive.

TABLE I

Characteristics of the 15 Distilling Columns as of 31 December 1946

*Number of distilling column**	*Rectifying section*			*Pot*		*Minimum operating residue (approx.)*	*Operating pressure drop*	*Operating through-put*	*Rate of collection of product*	*Operating reflux ratio (approx.)*	*Estimated number of theoretical plates at total reflux*
	Diameter	*Length*	*Packing†*	*Actual volume*	*Maximum charging capacity*						
	mm.	*metres*		*litres*	*litres*	*ml.*	*mm.Hg*	*ml./hour*	*ml./hour*		
1A	13	2·74	HG	3·2	2·7	60	12·7	300	2·0	150/1	150
2A	16	3·66	HG	7·2	6·0	100	19·2	720	4·0	180/1	200
3A	16	3·66	HG	7·2	6·0	100	19·2	720	4·0	180/1	200
4	16	3·66	HG	7·2	6·0	100	19·2	720	4·0	180/1	200
5	25	3·66	SSH	18·0	15·0	300	21·3	1,560	12·5	125/1	125
6	25	3·66	SSH	18·0	15·0	300	21·3	1,560	12·5	125/1	125
7	20	3·66	SSH	7·2	6·0	135	21·3	1,240	8·5	145/1	130
8	20	3·66	SSH	7·2	6·0	135	21·3	1,240	8·5	145/1	130
9	15	3·66	SSH	7·2	6·0	100	21·3	740	4·5	165/1	135
10	15	3·66	SSH	7·2	6·0	100	21·3	740	4·5	165/1	135
11A	16	3·66	HG	7·2	6·0	100	19·2	720	4·0	180/1	200
12	15	3·66	SSH	3·2	2·7	80	21·3	740	4·5	165/1	135
13	20	3·66	SSH	7·2	6·0	135	21·3	1,240	8·5	145/1	130
14	25	3·66	SSH	7·2	6·0	175	21·3	1,560	12·5	125/1	125
15A	16	3·66	HG	7·2	6·0	100	19·2	720	4·0	180/1	200

* The letter 'A' indicates that a new rectifying section was installed.

† SSH represents stainless steel helices, single turn, $\frac{3}{32}$ in. in diameter, made of No. 30 AWG wire[5]; HG represents Heligrid packing[3].

sine fractions of petroleum. This is because distillation can separate either by size or by type of molecule, according to whether one operates at a fixed pressure on the one hand, or alternately at two fixed pressures or azeotropically or extractively on the other hand. For each of the several kinds of distillation, except extractive distillation, the same distillation apparatus may be used, with substantially the same procedure.

In the distillation laboratory at the National Bureau of Standards there are 15 distilling columns in continuous operation, 24 hours per day, every day in the year. These columns have charging capacities ranging from ½ to 15 litres, with separating efficiencies in the range of 125 to 200 equivalent theoretical plates. The reflux ratios used range from 125/1 to 180/1, with rates of removal of product ranging from 2·0 to 12·5 ml. (liquid) per hour. The total time of distilling given charges ranges up to 2,000 hours of continuous operation. The characteristics of the 15 distilling columns in operation on 31 December 1946 are summarized in Table I. Fig. 1 shows a view of the distillation laboratory.

Distillation of material of the gasoline and kerosine ranges is performed at one of three pressures, which are controlled automatically at 725, 217, and 57 mm.Hg to ±0·1 mm.Hg. The first pressure was selected so as to be always below the lowest prevailing atmospheric pressure, and the second and third pressures were arbitrarily selected so as to produce successive lowerings of about 45° C. in the boiling-point of material of the gasoline and kerosine ranges. The important temperatures of the liquid-vapour equilibrium in the head of each distilling column are measured with platinum resistance thermometers with a sensitivity of 0·01° C. per mm. on the galvanometer scale, and an overall accuracy of ±0·01° C. Except in unusual cases, distillation temperatures for material of the kerosine range are not permitted to go above about 200° C.

In connexion with the requirement regarding the number of theoretical plates needed for a given distillation, Table II gives some approximate values of the minimum number of theoretical plates necessary to produce, from an equimolal ideal mixture of hydrocarbons *A* and *B*, the more volatile hydrocarbon *A* in a purity of 0·90, 0·99, and 0·999 mole fraction, respectively, when *A* and *B* are average hydrocarbons of the gasoline range having differences in normal boiling-point equal to 4, 2, and 1° C. and forming substantially ideal solutions.

Complete details of the distillation methods, equipment, and procedures have been described [95, 97].

TABLE II

Approximate Minimum Number of Theoretical Plates required in a Distillation Column to produce, from an Equimolal Mixture of A and B, the more Volatile Hydrocarbon A in given Degrees of Purity when A and B are Average Hydrocarbons of the Gasoline Range having differences in Boiling-point as indicated

Difference in normal boiling-points of A and B	*Composition*				*Approximate minimum number of equivalent theoretical plates required*
	Pot		*Head*		
	A	*B*	*A*	*B*	
°C.	*mole fraction*		*mole fraction*		
4	0·50	0·50	0·90	0·10	20
4	0·50	0·50	0·99	0·01	40
4	0·50	0·50	0·999	0·001	60
2	0·50	0·50	0·90	0·10	40
2	0·50	0·50	0·99	0·01	80
2	0·50	0·50	0·999	0·001	120
1	0·50	0·50	0·90	0·10	80
1	0·50	0·50	0·99	0·01	160
1	0·50	0·50	0·999	0·010	240

V. Distillation at different Pressures

When a mixture of hydrocarbons contains components that have substantially the same boiling-point at the normal distilling pressure but significantly different boiling-points at a different pressure, the separation of such components can be effected by distilling the mixture alternately at the two pressures. When the pressure is lowered from 760 to 100 mm.Hg, the corresponding lowering of the boiling-point for given types of hydrocarbons of the gasoline and kerosine ranges is greater than that of a normal paraffin of the same boiling-point at 760 mm.Hg by the following amounts: normal paraffins, 0° C.; isoparaffins, 0 to 2½° C.; cycloparaffins (naphthenes), 1½ to 4½° C.; alkyl benzenes, 0 to 2° C., and alkyl naphthalenes, 3 to 4° C. These relationships are illustrated graphically in Fig. 2 for some hydrocarbons. The foregoing differences in boiling-point, although not large, are sufficient to permit a good separation in distillation columns of 100 or more theoretical plates.

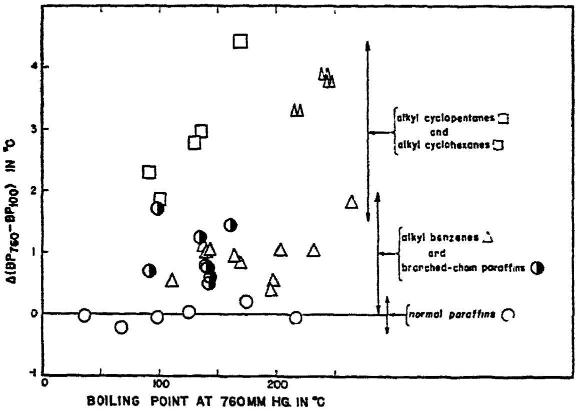


FIG. 2. Difference in the change of boiling-point with pressure for several types of hydrocarbons.

The scale of abscissae gives in °C. the value of the boiling-point of the given hydrocarbon at 760 mm.Hg. The scale of ordinates gives in °C. the value of

$$\Delta\,(BP_{760}-BP_{100}) = (BP_{760}-BP_{100})-(BP_{760}-BP_{100})\ n\text{-paraffin}$$

that is, the excess lowering of the boiling-point of a given hydrocarbon over that of a hypothetical *n*-paraffin of the same boiling-point at 760 mm.Hg. as the pressure is lowered from 760 to 100 mm.Hg.

As can be seen from the relationships given and from the fact that (see later) other processes are available for easily separating aromatics from paraffins and naphthenes (cycloparaffins), the great usefulness of the process of distilling alternately at two fixed pressures lies in the separation of paraffins from naphthenes and in separating dinuclear aromatics from mononuclear aromatics.

VI. Azeotropic and Extractive Distillation

When a substantially constant-boiling mixture of hydrocarbons contains components whose vapour pressures are affected differently by the addition of a non-hydrocarbon compound, the distillation of the hydrocarbons with the added compound may serve to separate the hydrocarbon components.

When the added compound is one which is relatively nonvolatile, compared to the hydrocarbons, the added compound will exist substantially entirely in the liquid phase and the process will be that of extractive distillation. In this case, the added compound must be introduced at the top of the column and be distributed through the rectifying section by gravity flow. The added substance must then be separated from the material in the pot and be pumped to the top of the column for recirculation through the rectifying section. Because of the necessity of using a more complicated apparatus with attendant increase in the cost of personnel for operation, the A.P.I. Research Project 6 has not used extractive distillation in its work, but has used instead azeotropic distillation which can be performed with exactly the same apparatus and procedure as for regular distillation.

In azeotropic distillation, the added compound is of the same general volatility as the compounds to be separated, and consequently can be introduced into the pot with the original charge. A further important advantage of azeotropic distillation is that an excess of the added substance may be used so that none of the wanted substances being separated need remain as hold-up or residue in the distillation column, but can all be taken overhead in the azeotropic distillate.

In general, for azeotropic distillation, the added nonhydrocarbon compound will be a polar organic compound (of about the same boiling-point as the hydrocarbons), which has the ability to form with each of the hydrocarbons a binary minimum constant-boiling (or azeotropic) mixture. The consequent lowering of the boiling-point will be greatest for the paraffin component, next greatest for the naphthene or cycloparaffin component, with the mononuclear aromatics and dinuclear aromatics following in that order.

For example, consider three hydrocarbons of different types normally boiling near the same temperature, as the following:

Compound	*Type*	*Normal boiling-point, °C.*
Benzene	Aromatic	80·1
Cyclohexane	Naphthene (cycloparaffin)	80·8
2,4-Dimethylpentane	Paraffin	80·8

One finds that ethyl alcohol, whose normal boiling-point is 78° C., forms with each of these three hydrocarbons a minimum-boiling azeotropic mixture, as follows:

Mixture	*Type of hydrocarbon*	*Boiling-point, °C.*
Benzene and ethyl alcohol	Aromatic	68
Cyclohexane and ethyl alcohol	Naphthene	64
2,4-Dimethylpentane and ethyl alcohol	Paraffin	62

Aromatic hydrocarbons may be separated from paraffins and naphthenes (cycloparaffins) with relative ease by azeotropic distillation, whereas the separation of paraffins from naphthenes is more difficult.

Fig. 3 illustrates the relationships of boiling-point and composition for the binary azeotropic mixtures formed between ethyl alcohol and a number of paraffin, naphthene, olefine, and aromatic hydrocarbons, and shows how the composition of the azeotropic mixture changes with the boiling-point of the members of a given homologous series of hydrocarbons. Data are given for isopentane, *n*-pentane, *n*-hexane, *n*-heptane, and *n*-octane of the paraffins, for cyclohexane and methylcyclohexane of the naphthenes, for 3-methylbutene-1 and 2-methylbutene-2 of the monoolefines, for 2-methylbutadiene-1,3 and hexadiene-1,5 for the diolefines, and for benzene and toluene of the aromatics. When the boiling-point of the hydrocarbon is considerably below that of the azeotrope-forming substance, the composition of the azeotropic mixture will be high in the given hydrocarbon, as shown for the two pentanes and the two pentenes. As the boiling-point of the hydrocarbon rises, the boiling-point of the azeotropic mixture, always below that of the hydrocarbon, moves towards the boiling-point of the pure azeotrope-forming substance, and the composition of the azeotropic mixture likewise becomes leaner in hydrocarbon, with both the boiling-point and the composition approaching those of the pure azeotrope-forming substance as a limit.

As this is the general behaviour of such systems, the dashed line, giving the loci of the points representing the boiling-point and composition of the binary azeotropic mixtures of ethyl alcohol with the paraffin hydrocarbons listed, can be used to estimate the boiling-point and composition of binary azeotropic mixtures of ethyl alcohol with other paraffin hydrocarbons of known boiling-point for which no data on azeotropic mixtures exist. It will be noted that the points for the other hydrocarbons fall above the line for the paraffin hydrocarbons approximately in the order—naphthenes, mono-olefines, diolefines, and aromatics. It appears that, with a given azeotrope-forming substance, all hydrocarbons of about the same boiling-point will form azeotropic mixtures having roughly the same composition in terms of mole fraction of the azeotrope-forming substance, and that the boiling-points of these same azeotropic mixtures usually will decrease in the order aromatic, diolefine, mono-olefine, naphthene, and paraffin. The same general relationships hold for the hydrocarbons with other azeotrope-forming substances.

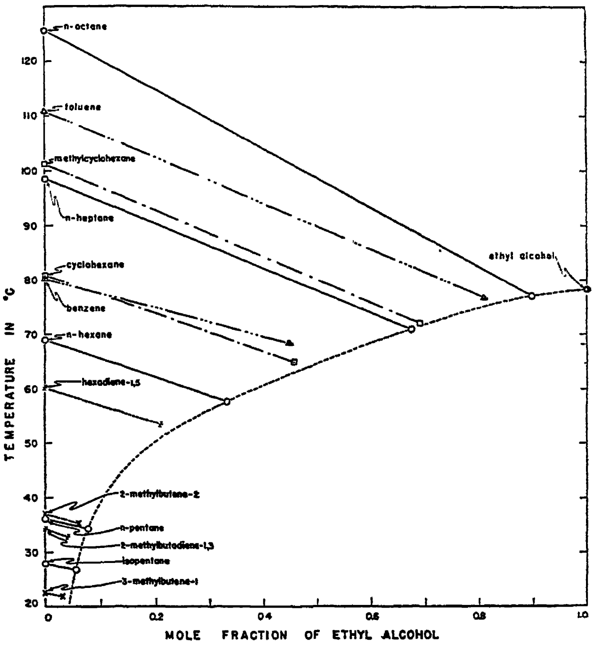


FIG. 3. Plot of the values of the boiling-point and composition of the binary azeotropic mixtures formed between ethyl alcohol and some paraffin, naphthene, olefine, and aromatic hydrocarbons, together with the boiling-points of the pure components.

The scale of ordinates gives the temperatures in °C., and the scale of abscissae gives the mole fraction of ethyl alcohol in the respective azeotropic mixtures. The straight lines are drawn to join the boiling-point and composition of the azeotropic mixture with the boiling-point of the corresponding hydrocarbon in the pure state. The curved dashed line gives the loci of points representing azeotropic mixtures of ethyl alcohol with paraffin hydrocarbons.

In the work of the A.P.I. Research Project 6 on the separation of hydrocarbons by azeotropic distillation on a laboratory scale, it is usually required of an azeotrope-forming substance that it (*a*) has a boiling-point near (not more than 30° or 40° C. away from) the boiling-range of the hydrocarbons to be separated; (*b*) is completely soluble in water and preferentially less soluble in the hydrocarbon at room temperature, in order that the removal of the azeotrope-forming substance from the hydrocarbon with which it is associated in the azeotropic distillate may be accomplished easily by extraction with water; (*c*) is completely soluble in the hydrocarbon at the distillation temperature and for some degrees below this in order that two phases shall not form in the condenser and reflux regulator and thus cause difficulty in the operation of the latter, and, where packed instead of bubble-cap columns are used, in order that the liquid phase in the rectifying section shall be entirely homogeneous, thus avoiding the possibility of irregular segregation of two liquid phases in the packed section; (*d*) is readily obtainable in a sufficiently pure state at reasonable cost; and (*e*) is non-reactive with hydrocarbons or with the material of which the still is constructed.

Among the large number of substances that are available for use in the azeotropic distillation of hydrocarbons, those that have been used in this laboratory include the following compounds, which boil (as pure substances) approximately at the temperatures given:

Compound	*Boiling-point °C. at 1 atm.*
Methyl alcohol	66
Ethyl alcohol	78
Methyl cyanide	82
Acetic acid	118
Ethylene glycol monomethyl ether	125
Ethylene glycol monoethyl ether	135
Ethylene glycol monomethyl ether acetate	144
Ethylene glycol monobutyl ether	171
Diethylene glycol monomethyl ether	194

In preparing for the separation of the hydrocarbons occurring in any given fraction of petroleum, it is necessary to have the mixture of hydrocarbons well separated by a systematic and efficient distillation into a series of substantially constant-boiling fractions prior to the azeotropic distillation. This is necessary in order to avoid having any paraffins mixed with lower-boiling naphthenes and, in turn, any paraffins and naphthenes mixed with lower-boiling aromatics, which kind of mixing will tend to nullify the separation normally attainable by the azeotropic distillation of mixtures of hydrocarbons of the same boiling-point. Furthermore, if the prior distillation is made at a pressure below the normal distilling pressure, the separation of the paraffins from the naphthenes will be enhanced.

Fig. 4 illustrates the results obtained in separating aromatics, naphthenes, and paraffins by azeotropic distillation, the separation being indicated by the change in refractive index with the amount of hydrocarbon recovered from the distillate. These distillations were performed as single-batch distillations in columns having a separating efficiency equivalent to about 100 theoretical plates.

Part I of Fig. 4 shows the separation obtained in the azeotropic distillation, with methyl cyanide (boiling-point 82° C.), of a mixture of toluene (boiling-point 110·6° C.) with a substantially constant boiling (110·0 to 110·5° C.) fraction of petroleum containing paraffin hydrocarbons with some naphthenes. The separation of toluene from these paraffin and naphthene hydrocarbons having substantially the same boiling-point is almost quantitative.

Part II of Fig. 4 shows the separation obtained in the azeotropic distillation, with ethylene glycol monobutyl ether (boiling-point 171° C.), of a narrow-boiling (166 to 169° C.) fraction of petroleum containing aromatic, naphthene, and paraffin hydrocarbons. This shows the almost complete separation of the aromatic hydrocarbons from the naphthenes and paraffins, and also a partial separation of the paraffins from the naphthenes.

Specific details of the application of the process of azeotropic distillation in isolating hydrocarbons from petroleum and in purifying compounds have been reported [8, 41, 52, 60, 61, 73, 74, 75, 77, 78, 94, 96, 100, 102, 105, 110].

VII. Extraction

The process of extraction may be used to separate a mixture of hydrocarbons that have significantly different solubilities in a given solvent at a given temperature. The distribution ratio of the hydrocarbons between the solvent

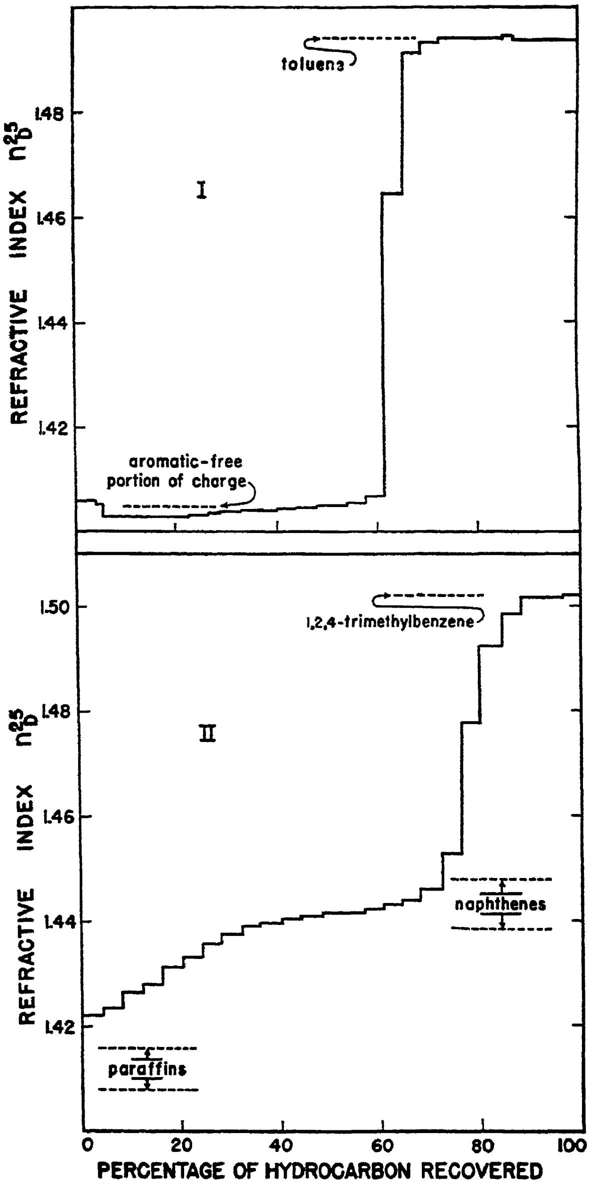


FIG. 4. Diagrams illustrating the separation of aromatic, naphthene, and paraffin hydrocarbons by azeotropic distillation.

The scale of ordinates gives the refractive index of the hydrocarbon recovered from the azeotropic distillate, and the scale of abscissae gives the percentage of the hydrocarbon recovered. The distillations were performed in a Bruun glass bubble-cap column of about 100 theoretical plates, with a reflux ratio of about 50 to 1. Part I shows the results of the azeotropic distillation, with methyl cyanide at atmospheric pressure, of a mixture of toluene (boiling-point 110·6° C.) with a narrow-boiling (110·0° to 110·5° C.) mixture of paraffins and naphthenes. The azeotropic distillate was by volume about 20% of hydrocarbon for the aromatic and about 25% for the paraffins and naphthenes. Part II shows the results of the azeotropic distillation, with ethylene glycol monobutyl ether at 770 mm., of the mixture of aromatic, naphthene, and paraffin hydrocarbons naturally occurring in a narrow-boiling (166° to 169° C.) fraction of Oklahoma petroleum. The azeotropic distillate was by volume about 60% of hydrocarbons, increasing from aromatic to naphthene to paraffin.

EXTRACTOR FOR SOLVENTS LIGHTER THAN OIL

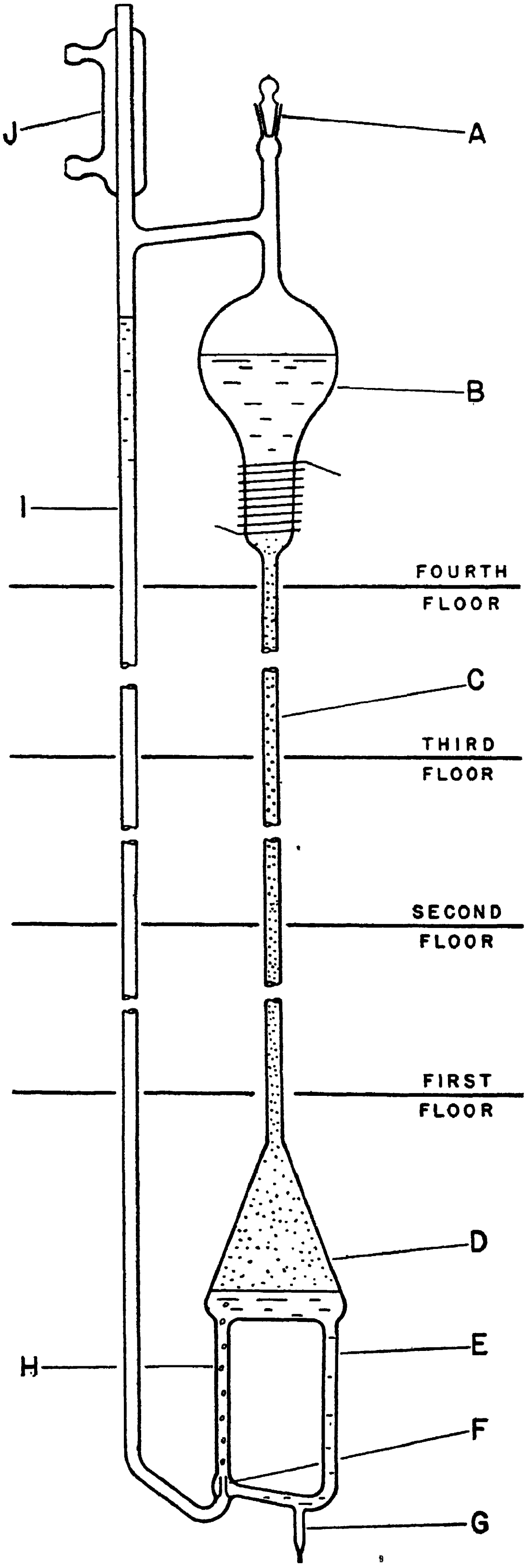


FIG. 5. Schematic diagram of tall extraction apparatus for solvents lighter than the hydrocarbons to be separated. See text for description.

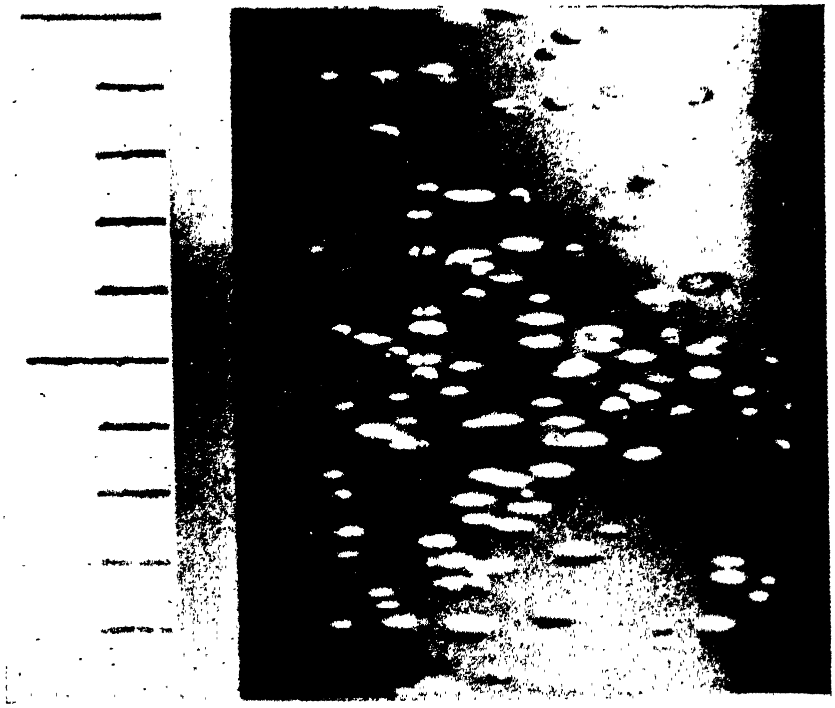


FIG. 6. Enlarged section of the reflux arm of the extraction apparatus given in Fig. 5, showing the globules of the hydrocarbon phase. The scale at the left is in mm.

phase and the hydrocarbon phase may be altered by changing the solvent or the temperature or both. For the best results an apparatus having a separating efficiency equivalent to many theoretical stages, and operated with reflux, is used. Solvents that have been used extensively in this work include liquid sulphur dioxide, acetone, methyl cyanide, and methyl formate.

Fig. 5 shows a laboratory apparatus 46 ft. high that was used with a solvent lighter than the hydrocarbons to be separated [48]. In operation the solvent in *B* is distilled into the left side of the apparatus, condenses, in *J*, and when a given head of liquid is reached, the solvent begins to pass from *I* through *F* and the hydrocarbon phase *E*. As it passes through the hydrocarbon phase, the solvent dissolves the more soluble components of the mixture of hydrocarbons, and the solvent phase then ascends to the boiler *B*. As the solvent is removed here, the solvent phase becomes saturated with hydrocarbons and from there on the less soluble hydrocarbons precipitate from this solution in the form of fine globules that fall through the ascending solvent phase. Fig. 6 gives an enlarged section of this column, showing the fine globules of hydrocarbon phase descending through the ascending solvent phase. After a time the solution in the boiler *B* will contain the most soluble part of the original mixture of hydrocarbons, and fractions are withdrawn here at appropriate intervals. The solution withdrawn is replaced with fresh solvent.

When the solvent is heavier than the hydrocarbons to be separated, in which case the hydrocarbon globules must travel upward instead of downward, the reflux may be produced by refrigerating the bottom of the left arm so that the precipitated hydrocarbon phase ascends in fine globules and the hydrocarbons that are retained in solution pass across into the right arm of the apparatus to be removed as product at an appropriate time [58]. Three 55-ft. columns of this latter type have been used on aromatic-free material of the kerosine fraction to separate paraffins from naphthenes (more soluble) by selective extraction with reflux, with methyl formate as the solvent at a temperature near 10° C.

When one of the components of a mixture does not form a second phase with the solvent (except at temperatures too low to be practical, as is the case with methyl cyanide and aromatic hydrocarbons of the kerosine region), the required second liquid phase may be formed by the use of an appropriate second solvent. In the separation of the distillate in the range from 200 to 230° C. into an aromatic portion and a paraffin-naphthene portion, methyl cyanide was used as one solvent and a commercial aromatic-free mixture of paraffins and naphthenes ('Marcol', initial boiling-point about 230° C. at 57 mm.Hg) was used as the other solvent.

The apparatus used in the extraction process is shown diagrammatically in Fig. 7. Referring to this figure, kerosine is contained in reservoir *B* and is allowed to flow at a controlled rate through glass valve *D* to the top of rotating shaft *F*. It then flows down the hollow shaft to the enlargement in the distributor *J* and is there forced through small holes and dispersed in the form of small globules in the solvent contained in the column *K*. These globules fall to the bottom of the column and form a layer which is withdrawn intermittently through the valve *N*. The solvent is contained in reservoir *B′* and is admitted at a controlled rate through glass valve *D′* and tube *O* to the bottom of the column. The extract portion flows through tube *I* (where small globules of oil have an opportunity to settle out and return to the column) to a collecting bottle.

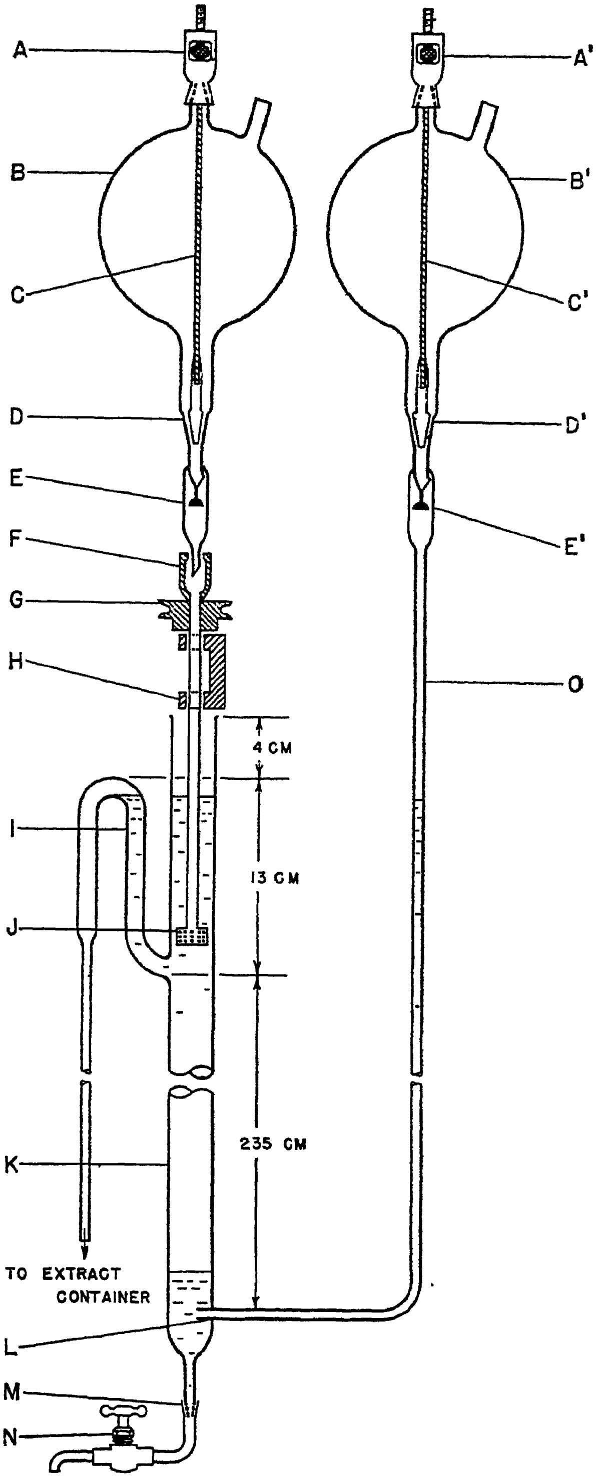


FIG. 7. Apparatus for extracting aromatic hydrocarbons from the kerosine fraction of petroleum. See text for description.

The extraction procedure is illustrated schematically in Fig. 8. Extractors 1 and 2 were operated in series. In extractor 1 partially extracted kerosine from extractor 2 was re-extracted with fresh methyl cyanide and yielded kerosine raffinate fractions with values for the specific dispersion of about 100, which indicated the presence of about 2·5 % of aromatic hydrocarbons. The methyl cyanide extract from extractor 1 was used as solvent in extractor 2 with the original kerosine. In extractor 3 the methyl cyanide extract was re-extracted with Marcol and yielded a methyl cyanide extract substantially free from naphthenes and paraffins. The Marcol, however, dissolved some aromatic hydrocarbons in addition to the naphthene and paraffin hydrocarbons, so that it was necessary to separate these kerosine hydrocarbons from the Marcol by distillation and recycle them as shown in Fig. 5.

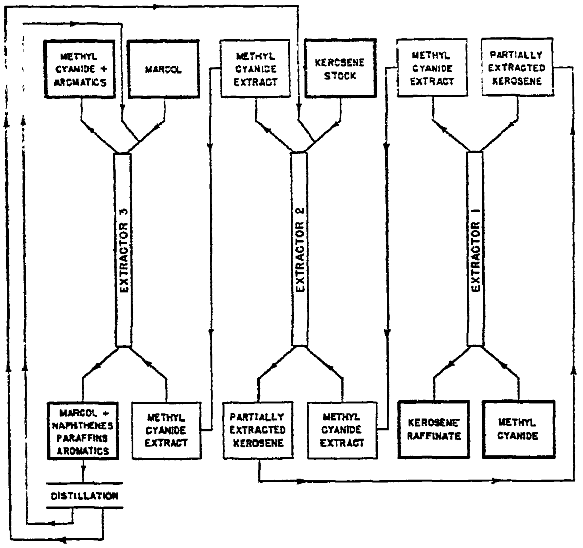


FIG. 8. Schematic diagram of the extraction process used to separate the aromatic hydrocarbons from the paraffin and naphthene hydrocarbons in the kerosine fraction.

Unlike the process of azeotropic distillation, the process of extraction will, within certain limits, operate successfully on relatively wide-boiling mixtures of hydrocarbons. Specific applications of the process of extraction in the separation of hydrocarbons from petroleum have been reported [19, 43, 48, 58, 63, 73].

VIII. Adsorption

The fractionating process of adsorption operates on differences in adsorbability among the components being separated. With adsorption from the liquid phase, this process may be used on hydrocarbons of both low and high molecular weight. Aromatic hydrocarbons may easily be separated from paraffins and naphthenes, because of the relatively much greater adsorbability of the aromatics, and such separations may be made successfully on extremely wide-boiling mixtures. The separation, by adsorption, of paraffins from naphthenes, aromatics from aromatics, naphthenes from naphthenes, and paraffins from paraffins, is much more difficult.

Since 1934, the A.P.I. Research Project 6 at the National Bureau of Standards has made use of the fractionating process of adsorption in its work on the separation and purification of hydrocarbons [40, 43, 60, 63, 70, 73, 81, 83, 85, 86, 90, 99, 103, 106]. The early work showed the effectiveness of adsorption with silica gel in separating aromatic hydrocarbons from paraffins and naphthenes including hydrocarbons of low molecular weight and of high molecular weight. The process was also found convenient for removing water and other non-hydrocarbon impurities from purified hydrocarbons. Small but significant fractionation by adsorption was found to occur between paraffins and cycloparaffins and between *n*-paraffins of different molecular weight. Methods for the analysis of aromatic hydrocarbons (and some olefines) were developed, as well as for the quantitative separation of aromatic hydrocarbons on a large laboratory scale. Recently the newer analytical method has been extended to large-scale separations and to the investigation of the relations between adsorbability and molecular structure among hydrocarbons having nearly the same adsorbability.

With the first method for the separation of aromatic hydrocarbons from paraffins and naphthenes, by adsorption, the mixture is introduced into the top of a column containing an appropriate excess of silica gel. A low-boiling paraffin hydrocarbon diluent, such as *n*-pentane, is then added in sufficient quantity to remove from the column the paraffin and naphthene hydrocarbons, leaving the aromatic hydrocarbons remaining on the adsorbent. The aromatic hydrocarbons, together with the added diluent, are then removed by adding a desorbing liquid, such as methanol, ethanol, or isopropanol. The paraffins and naphthenes, together with pentane, are thus obtained as a mixture from which the pentane is easily removed by distillation. The aromatic hydrocarbons are obtained as a mixture with the pentane and the alcohol used for desorbing. The alcohol is readily removed by extraction with water and the pentane by distillation. With this procedure a comparatively coarse silica gel, most of which passes a no. 28 sieve but is retained on a no. 200 sieve, may be used. With this size of silica gel and with material of the gasoline range, filtration is sufficiently rapid without the application of external pressure to force the liquids through the column. The column itself may consist of a glass tube drawn down and sealed to a stopcock at the bottom, and fitted with a plug of glass wool to serve as a retainer for the adsorbent. About 15 to 20 g. of silica gel is required for each ml. of aromatic hydrocarbon separated. The column may have a diameter up to 4 in., with a length at least 30 times the diameter.

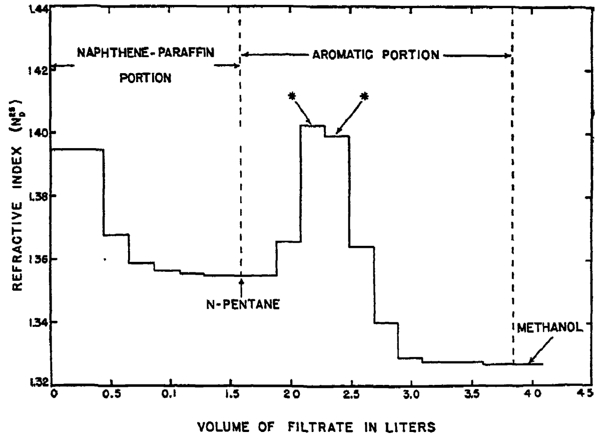


FIG. 9. Results of an experiment illustrating the separation of aromatic hydrocarbons from paraffins and naphthenes by adsorption.

The scale of ordinates gives the refractive index, N_D at 25° C., of the filtrate, and the scale of abscissae gives the volume of filtrate in litres. *n*-Pentane was used as the diluent and methanol as the desorbent.

Fig. 9 shows the results of a typical experiment. The refractive indices of the filtrate fractions decrease from the refractive index of the original naphthene-paraffin portion to that of *n*-pentane, then increase as aromatic hydrocarbons appear in the filtrate, and finally, when all the aromatic hydrocarbons have been removed, decrease nearly to the refractive index of the alcohol.

With the second method of utilizing the process of adsorption, the mixture of hydrocarbons is introduced into the top of a column of silica gel and, when the liquid level just reaches the top of the silica gel, a suitable desorbing liquid, such as ethyl or isopropyl alcohol, is added. The desorbing liquid forces the hydrocarbons down the column, during which passage the hydrocarbons are fractionated according to their adsorbability. The paraffins plus naphthenes issue from the column first, then come the aromatic hydrocarbons, followed by the desorbing liquid. Only a small first intermediate fraction, consisting of a mixture of paraffins, naphthenes, and aromatics, and a small second intermediate fraction consisting of aromatics and alcohol, is obtained. The advantage of this method is that there is no diluent to remove. With this procedure a fine silica gel, of particle size such that approximately 60% passes the no. 200 sieve and is retained on the no. 325 sieve, is required. To obtain a reasonable rate of filtration, pressure must be applied to force the liquid down through the adsorbent. With material of the gasoline range, in short columns (3 to 6 ft. in length), gauge pressures of 5 to 10 lb. per sq. in. are required. With more viscous material, in longer columns, higher pressures are required. Pressures up to 100 lb. per sq. in. have been used in this work.

This method is suitable for the determination of the aromatic content of mixtures containing aromatic, naphthene, and paraffin hydrocarbons. For such analyses small fractions of filtrate are collected, their refractive indices measured, and the fraction of the total volume constituted by the aromatic and by the paraffin-naphthene constituents, respectively, is determined. A 4-ft. analytical adsorption column, which will separate about 15 to 20 ml. of aromatic hydrocarbon, is shown in Fig. 10. Results of experiments, using this column with several synthetic mixtures, with an aviation fuel, and with a kerosine fraction, are shown in Figs. 11, 12, 13, and 14.

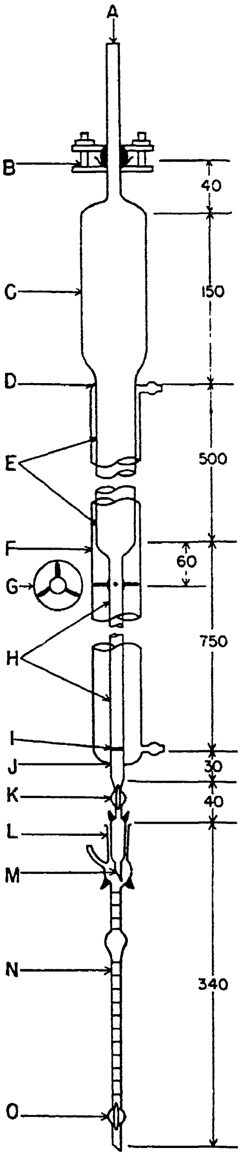


FIG. 10. Analytical adsorption column for determining the aromatic content of gasoline or kerosine fractions of petroleum.

This column, of Pyrex glass, is approximately 4 ft. in length.

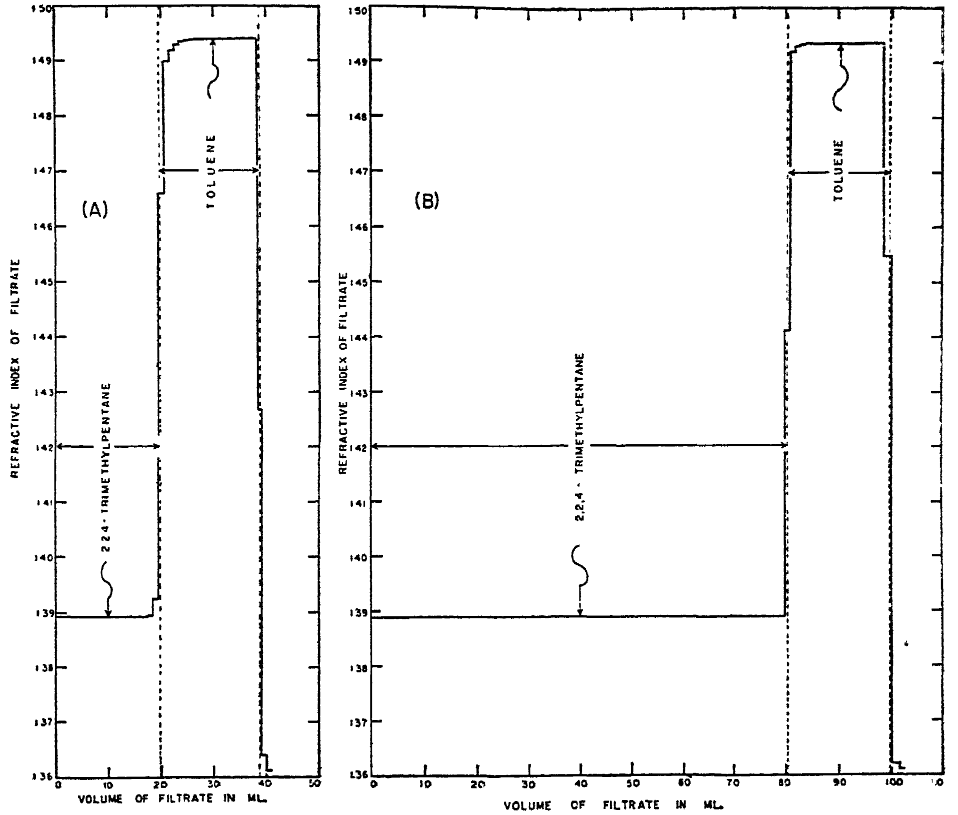


FIG. 11. Analyses, by adsorption, of mixtures containing aromatic and paraffin hydrocarbons.

The scale of ordinates gives the refractive index, N_D at 25° C., of the filtrate, and the scale of abscissae gives the volume of the filtrate in ml. A, an analysis in which approximately 40 ml. of a solution containing 49 and 51% by volume of toluene and 2,2,4-trimethylpentane, respectively, was used; B, an analysis in which approximately 100 ml. of a solution containing 19·6 and 80·4% by volume of toluene and 2,2,4-trimethylpentane, respectively, was used.

For the investigation of the relations between adsorbability and molecular structure among hydrocarbons having nearly the same adsorbability, a 26-ft. column similar in design to the column shown in Fig. 10, except for the additional length, is used. Results obtained on seven binary mixtures with this column are given in Figs. 15 to 21.

For larger-scale separations a 52-ft. stainless steel adsorption column with an inside diameter of ¾ in. is used. This column, which is provided with electrical heating units and an insulated jacket for use in reactivating the adsorbent in position, holds about 3·7 kg. of silica gel and will separate about 500 ml. of aromatic hydrocarbons in a single pass. The results of two experiments, one with a synthetic mixture, the other with a kerosine fraction distilling, at 1 atm., between 230° and 240° C., are shown in Figs. 22 and 23.

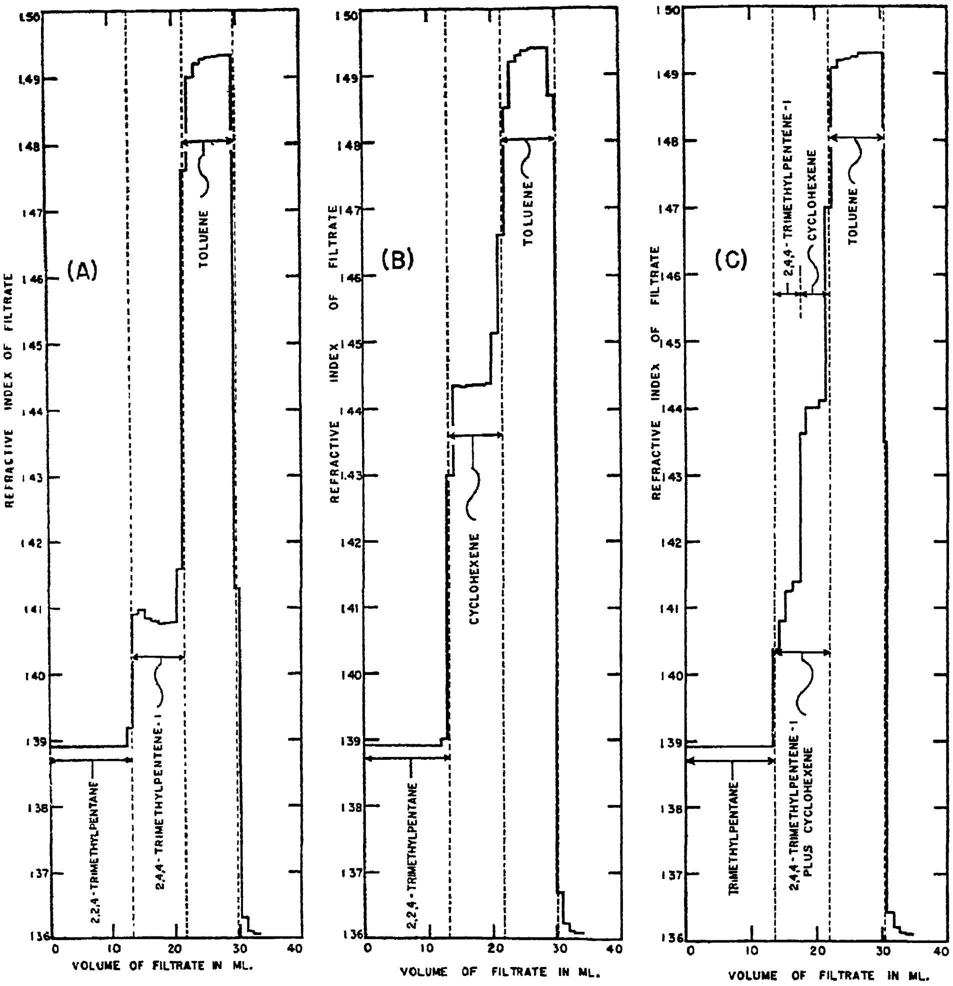


Fig. 12. Analyses, by adsorption, of solutions containing aromatic, monoolefine, and paraffin hydrocarbons.

The scale of ordinates gives the refractive index, N_D at 25° C., of the filtrate, and the scale of abscissae gives the volume of the filtrate in ml. A, an analysis in which approximately 25 ml. of a solution containing equal volumes of toluene, 2,4,4-trimethyl-1-pentane, and 2,2,4-trimethylpentane was used; B, an analysis in which approximately 25 ml. of a solution containing equal volumes of toluene, cyclohexane, and 2,2,4-trimethylpentane was used; C, an analysis in which approximately 25 ml. of a solution containing one-third toluene, one-sixth cyclohexene, one-sixth 2,4,4-trimethyl-1-pentane, and one-third 2,2,4-trimethylpentane was used. In all three analyses 5 ml. of 2,2,4-trimethylpentane was introduced into the adsorption column prior to the introduction of the solution.

As shown in Figs. 16, 17, 20, and 21, some binary mixtures of hydrocarbons are fractionated unsymmetrically to give a first filtrate fraction enriched in the less strongly adsorbed component (sometimes with the less strongly adsorbed component pure or nearly pure, as in Figs. 16, 17, and 20) with a break to a mixture of the two components which, while richer in the more strongly adsorbed component, does not fractionate further or fractionates only slightly. For such non-fractionating mixtures it is apparent that the two components exist in the liquid phase in a ratio in which the fugacity or escaping tendency of each component is equal to its fugacity or escaping tendency from the phase adsorbed on the solid. Other binary mixtures, as shown in Figs. 15, 18, and 19, are fractionated symmetrically or nearly so and may give both components in a pure condition (Fig. 19). For such mixtures, which do not possess a composition which is non-fractionating, both components may be obtained in a substantially pure condition provided adequate length of fractionating section is employed.

With regard to the influence of molecular size and structure on adsorbability, the several structural components, in order of decreasing adsorbability, may be listed as (*a*) dinuclear or polynuclear aromatic, (*b*) phenyl, and (*c*) cycloparaffin and paraffin, with (*a*) and (*b*) being as a class very much more strongly adsorbed than (*c*). That is to say, the addition of a phenyl group to a paraffin or cycloparaffin group produces a molecule having an adsorbability in the class of (*a*) and (*b*), whereas the differences in adsorbability among cyclopentyl, cyclohexyl, *n*-alkyl, and isoalkyl are relatively small. With hydrocarbons having nearly the same adsorbability, for adsorption from equivalent concentrations in the liquid phase, with silica gel as the adsorbent, the following relations appear to hold:

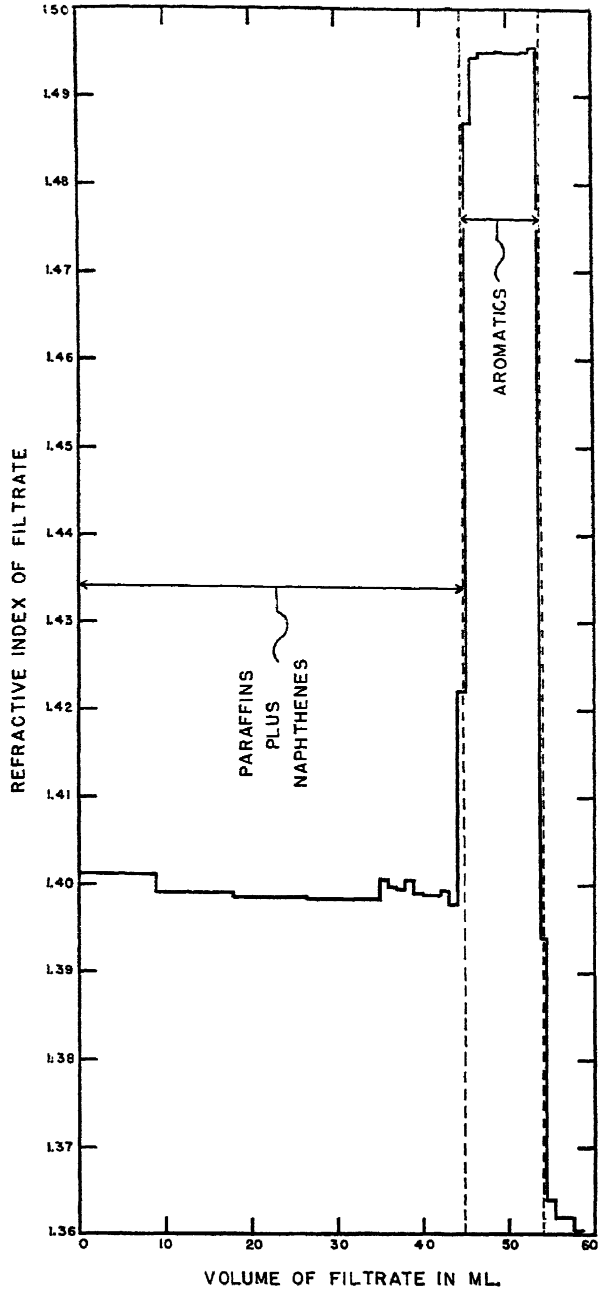


FIG. 13. Analysis, by adsorption, of an aviation gasoline.

The scale of ordinates gives the refractive index, N_D at 25° C., of the filtrate, and the scale of abscissae gives the volume of the filtrate in ml. The plot refers to an analysis in which approximately 55 ml. of an aviation gasoline was used.

(*a*) Increasing the number of carbon atoms in a *n*-alkyl group decreases the adsorbability. This is true whether the given *n*-alkyl group is already attached to a phenyl, cyclopentyl, cyclohexyl, *n*-alkyl, or isoalkyl group.

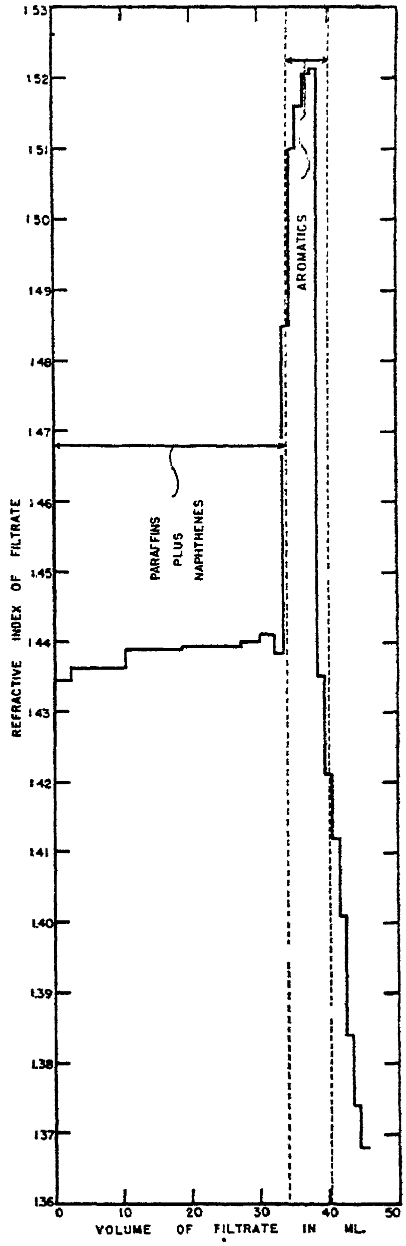


FIG. 14. Analysis, by adsorption, of a kerosine fraction.

The scale of ordinates gives the refractive index, N_D at 25° C., of the filtrate, and the scale of abscissae gives the volume of the filtrate in ml. The plot refers to an analysis in which approximately 40 ml. of a kerosine sample (b.p. 166° to 290° C.) was used.

(*b*) Cyclopentane is more strongly adsorbed than cyclohexane.

(*c*) A given alkyl cyclopentane is more strongly adsorbed than the corresponding alkylcyclohexane.

(*d*) With the same number of carbon atoms, a normal paraffin is more strongly adsorbed than an isoparaffin.

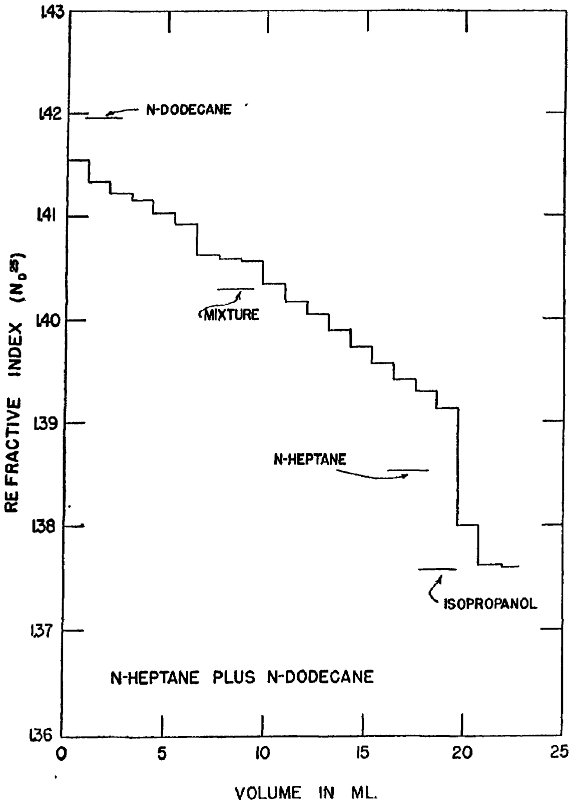


FIG. 15. Results of an experiment in the 26-ft. adsorption column with silica gel and a 50–50 mixture, by volume, of *n*-heptane and *n*-dodecane.

The scale of ordinates gives the refractive index, N_D at 25° C., of the filtrate and the scale of abscissae gives the volume of filtrate in ml. The desorbing liquid was isopropanol.

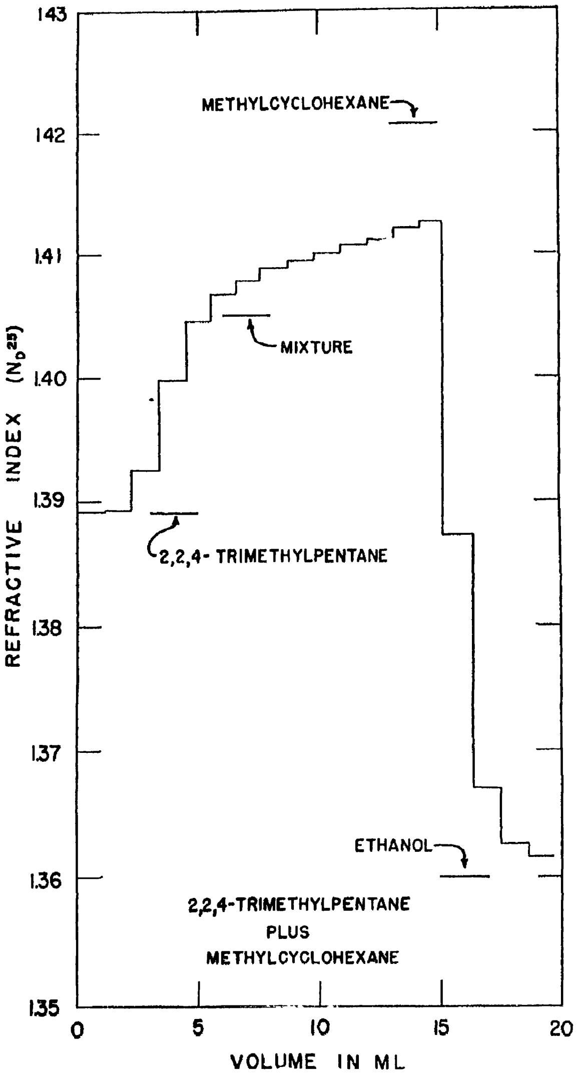


FIG. 16. Results of an experiment in the 26-ft. adsorption column with silica gel and a 50–50 mixture, by volume, of 2,2,4-trimethylpentane and methylcyclohexane.

The scale of ordinates gives the refractive index, N_D at 25° C., of the filtrate and the scale of abscissae the volume of filtrate in ml. The desorbing liquid was ethanol.

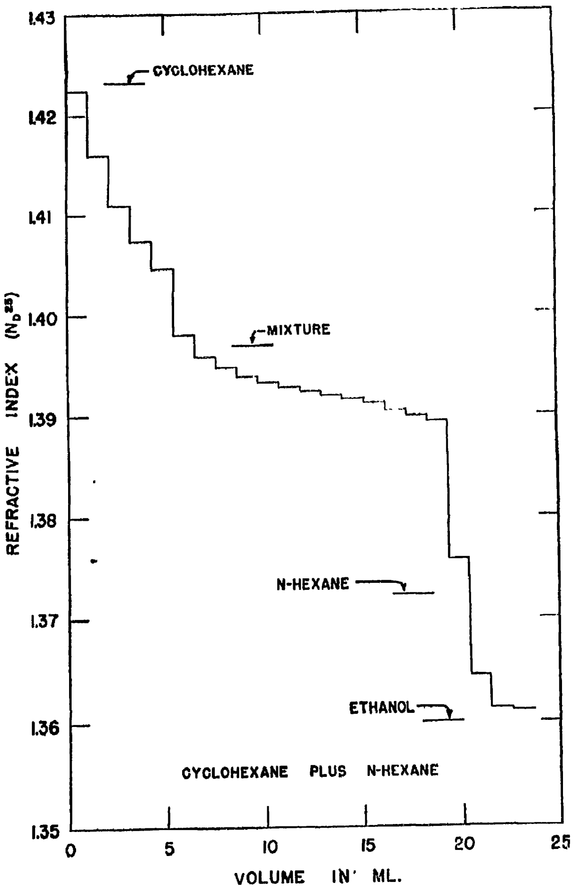


FIG. 17. Results of an experiment in the 26-ft. adsorption column with silica gel and a 50–50 mixture, by volume, of *n*-hexane and cyclohexane.

The scale of ordinates gives the refractive index, N_D at 25° C., of the filtrate and the scale of abscissae gives the volume of filtrate in ml. The desorbing liquid was ethanol.

(*e*) *n*-Hexane is more strongly adsorbed than cyclohexane.

(*f*) With the same number of carbon atoms, a *n*-alkyl cyclohexane is more strongly adsorbed than a normal paraffin.

(*g*) With the same number of carbon atoms per molecule, a poly-alkylbenzene is more strongly adsorbed than a normal alkylbenzene.

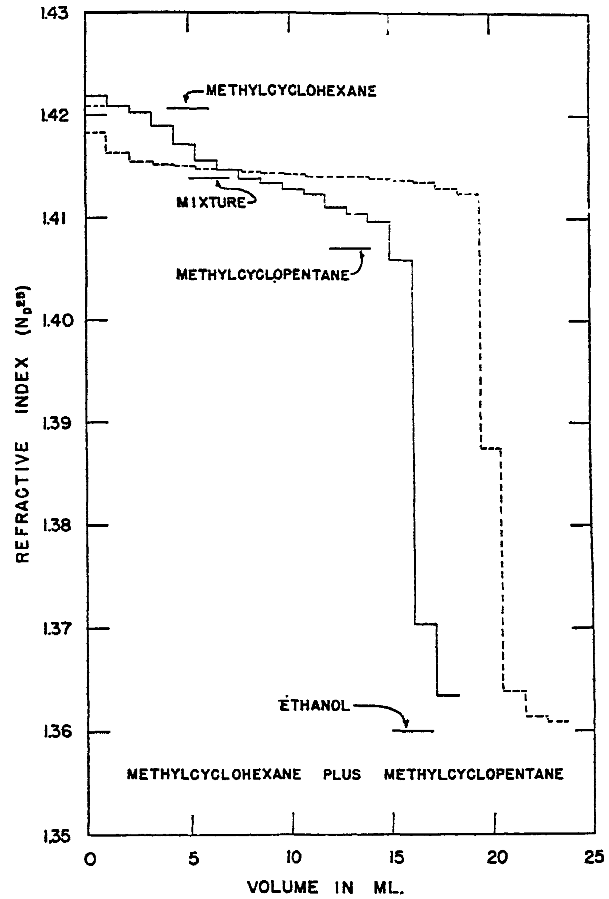


FIG. 18. Results of experiments in the 26-ft. and the 4-ft. adsorption columns with silica gel and a 50–50 mixture, by volume, of methylcyclopentane and methylcyclohexane.

The scale of ordinates gives the refractive index, N_D at 25° C., of the filtrate and the scale of abscissae gives the volume of filtrate in ml. The desorbing liquid was isopropanol. The solid line gives the results of the experiment in the 26-ft. column and the broken line those of the experiment in the 4-ft. column.

IX. Crystallization

The process of crystallization is generally used to increase the purity of a hydrocarbon that has been concentrated by means of one or more of the other fractionating processes. The most frequently used procedure is to mix the hydrocarbon with the proper amount of suitable solvent, take the mixture (usually with refrigeration) to a temperature that produces a 'mush' or 'slurry' of liquid with crystals of the wanted hydrocarbon, and then at this temperature to centrifuge the liquid from the crystals. In some cases, especially when it is sufficiently fluid near its melting-point, the liquid hydrocarbon may be processed without solvent, and the crystals are freed from the mother liquor by centrifuging as before.

X. Determination of Physical Properties

After a given hydrocarbon has been separated from petroleum in the manner described, a number of physical properties are measured for record and identification. These properties include the boiling-point, freezing-point, density, refractive index, and refractive dispersion. When the identity of the compound is not known, determinations of the molecular weight and the carbon-hydrogen content are also made. Other properties that are sometimes determined for purposes of record include viscosity, critical solution temperatures, and the infra-red, ultra-violet, or Raman spectra. Descriptions of apparatus for measuring the physical properties of hydrocarbons have been reported [91, 92, 93, 94].

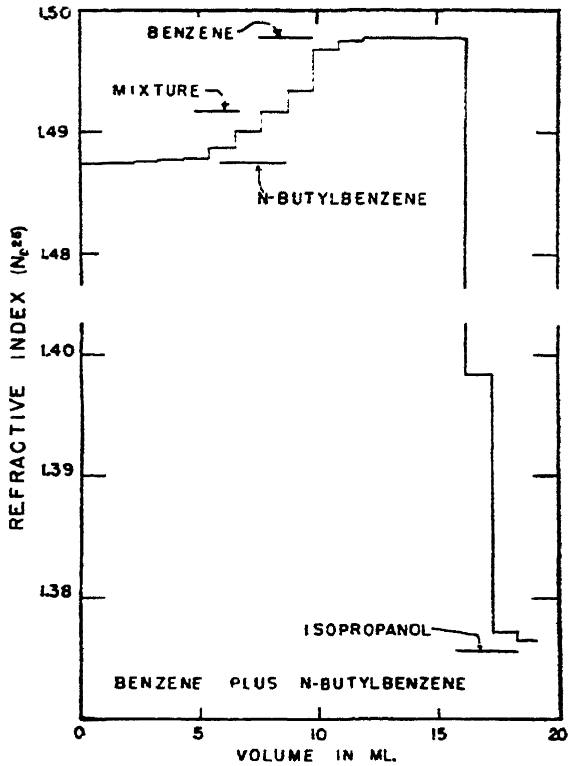


FIG. 19. Results of an experiment in the 26-ft. column with silica gel and a 50–50 mixture, by volume, of benzene and *n*-butylbenzene.

The scale of ordinates gives the refractive index, N_D at 25° C., of the filtrate, and the scale of abscissae gives the volume of the filtrate in ml. The desorbing liquid was isopropanol.

XI. Determination of Purity

Any rational method of purification will leave in a hydrocarbon only those impurities that have properties close to those of the given hydrocarbon, and such impurities tend to form an ideal solution with it. Furthermore, such impurities seldom form solid solutions with the given hydrocarbon. The ideal solution laws may therefore be applied to freezing and melting observations on such systems to ascertain quantitatively the amount of the unknown impurity. No property other than the freezing-point can be so interpreted into concentration of impurity when the impurity is unknown.

The amount of impurity in the purest lot of the hydrocarbon is determined by means of time–temperature freezing and melting curves. With appropriate apparatus, and

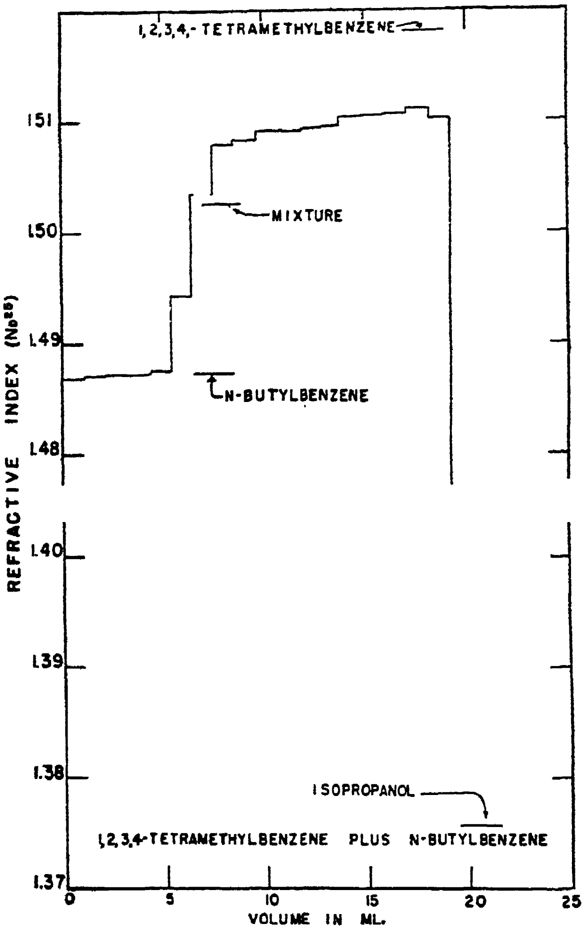


FIG. 20. Results of an experiment in the 26-ft. column with silica gel and a 50–50 mixture, by volume, of *n*-butylbenzene and 1,2,3,4-tetramethylbenzene.

The scale of ordinates gives the refractive index, N_D at 25° C., of the filtrate and the scale of abscissae gives the volume of filtrate in ml. The desorbing liquid was isopropanol.

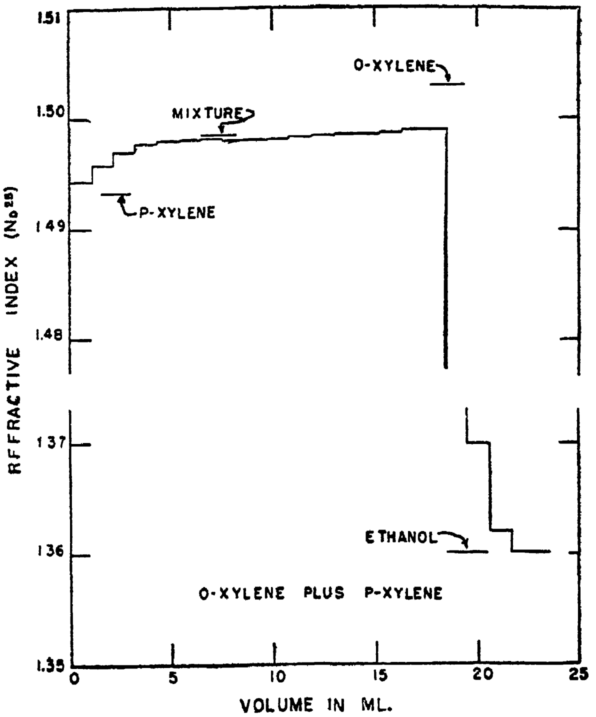


FIG. 21. Results of an experiment in the 26-ft. column with silica gel and a 50–50 mixture, by volume, of *p*-xylene and *o*-xylene.

The scale of ordinates gives the refractive index, N_D at 25° C., of the filtrate and the scale of abscissae gives the volume of the filtrate in ml. The desorbing liquid was ethanol.

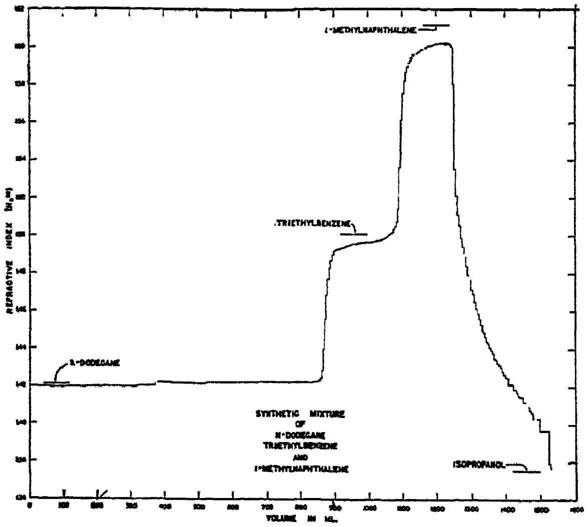


FIG. 22. Results of an experiment in the 52-ft. stainless steel column with silica gel and a known mixture of *n*-dodecane, triethylbenzene, and *l*-methylnaphthalene.

The scale of ordinates gives the refractive index, N_D at 25° C., of the filtrate and the scale of abscissae gives the volume of the filtrate in ml. The desorbing liquid was isopropanol.

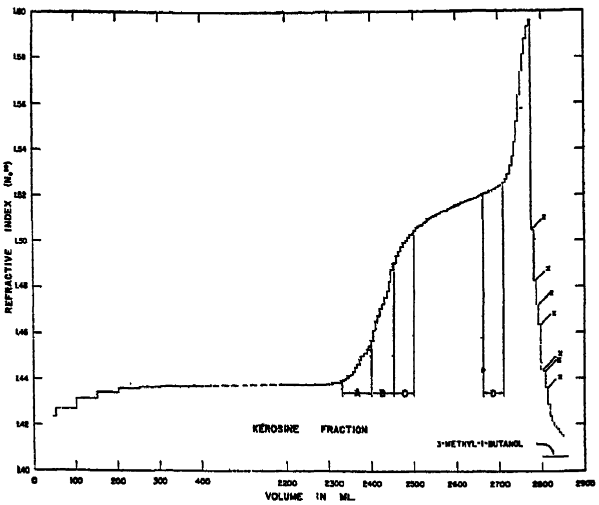


FIG. 23. Results of an experiment in the 52-ft. stainless steel column with silica gel and a kerosine fraction which distilled, at 1 atmosphere, between 230° and 240° C.

The scale of ordinates gives the refractive index, N_D at 25° C., of the filtrate and the scale of abscissae gives the volume of the filtrate in ml. The desorbing liquid was 3-methyl-1-butanol.

a thermometric system having a sensitivity of 0·001° C. per mm. on the scale, this procedure can be used to determine the amount of impurity with a sensitivity of 0·0001 in mole fraction. A large number of hydrocarbons isolated from petroleum in this work have contained 0·01 or less mole fraction of impurity.

Complete details of the apparatus and procedures for determining purity by measurement of freezing-points have been reported [76, 92].

XII. Oklahoma Petroleum Investigated

The large quantity of one representative crude petroleum which has been under investigation by the A.P.I. Research Project 6 was obtained [66] in 1928 from the Brett no. 6 well in the Ponca City field, in Oklahoma, through the courtesy of the Marland Oil Company (now part of the Continental Oil Company). The exact location of this well is in the centre of the NE. 1/4 SE. 1/4 of section 8, Township 25 North, Range 2 East, Kay County, Oklahoma. This well, located near the crest of the Ponca anticlinal structure, produced oil from the uppermost part of the Wilcox sand formation of the Simpson group, Middle Ordovician in age. The top of the producing horizon was encountered at a depth of 3,865 ft., the total depth of the hole being 3,872 ft. The Brett no. 6 well, brought in as a producer under its own gas pressure on 14 July 1919, was placed on the pump on 21 January 1926, and produced under vacuum until 26 October 1936, when the well was plugged and abandoned because of salt-water encroachment.

TABLE III

Hydrocarbons separated from Ponca, Okla., Petroleum as of 31 December 1946

Formula	*Name*	*Type*	*B.P., °C.*	*Formula*	*Name*	*Type*	*B.P., °C.*
CH_4	Methane	Paraffin	−161·5	C_9H_{18}	1,2,4-Trimethylcyclohexane	Cycloparaffin	141·2
C_2H_6	Ethane	Paraffin	− 88·6	C_9H_{20}	4-Methyloctane	Paraffin	142·5
C_3H_8	Propane	Paraffin	− 42·1	C_9H_{20}	2-Methyloctane	Paraffin	143·3
C_4H_{10}	Isobutane	Paraffin	− 11·7	C_9H_{20}	3-Methyloctane	Paraffin	144·2
C_4H_{10}	*n*-Butane	Paraffin	− 0·5	C_8H_{10}	*o*-Xylene	Aromatic	144·4
C_5H_{12}	2-Methylbutane	Paraffin	27·9	C_9H_{18}	Monocyclic†	Cycloparaffin	145·6
C_5H_{12}	*n*-Pentane	Paraffin	36·1	C_9H_{16}	Bicyclic†	Cycloparaffin	146·7
C_5H_{10}	Cyclopentane	Cycloparaffin	49·3	C_9H_{20}	*n*-Nonane	Paraffin	150·8
C_6H_{14}	2,3-Dimethylbutane	Paraffin	58·0	C_9H_{12}	Isopropylbenzene	Aromatic	152·4
C_6H_{14}	2-Methylpentane	Paraffin	60·3	C_9H_{12}	*n*-Propylbenzene	Aromatic	159·2
C_6H_{14}	3-Methylpentane	Paraffin	63·3	C_9H_{12}	1-Methyl-3-ethylbenzene	Aromatic	161·3
C_6H_{14}	*n*-Hexane	Paraffin	68·7	C_9H_{12}	1-Methyl-4-ethylbenzene	Aromatic	162·0
C_6H_{12}	Methylcyclopentane	Cycloparaffin	71·8	C_9H_{12}	1,3,5-Trimethylbenzene	Aromatic	164·7
C_7H_{16}	2,2-Dimethylpentane	Paraffin	79·2	C_9H_{12}	1-Methyl-2-ethylbenzene	Aromatic	165·1
C_6H_6	Benzene	Aromatic	80·1	$C_{10}H_{22}$	4-Methylnonane	Paraffin	165·7
C_6H_{12}	Cyclohexane	Cycloparaffin	80·7	$C_{10}H_{22}$	2-Methylnonane	Paraffin	166·8
C_7H_{14}	1,1-Dimethylcyclopentane	Cycloparaffin	87·8	$C_{10}H_{22}$	3-Methylnonane	Paraffin	167·8
C_7H_{16}	2-Methylhexane	Paraffin	90·0	C_9H_{12}	1,2,4-Trimethylbenzene	Aromatic	169·3
C_7H_{14}	*trans*-1,3-Dimethylcyclopentane	Cycloparaffin	90·8	$C_{10}H_{22}$	*n*-Decane	Paraffin	174·1
C_7H_{14}	*trans*-1,2-Dimethylcyclopentane	Cycloparaffin	91·9	C_9H_{12}	1,2,3-Trimethylbenzene	Aromatic	176·1
C_7H_{16}	3-Methylhexane	Paraffin	92·0	$C_{11}H_{16}$	Alkylbenzene*	Aromatic	204·1
C_7H_{16}	*n*-Heptane	Paraffin	98·4	$C_{10}H_{14}$	1,2,3,4-Tetramethylbenzene	Aromatic	205·0
C_7H_{14}	Methylcyclohexane	Cycloparaffin	100·9	$C_{11}H_{16}$	Alkylbenzene*	Aromatic	206·6
C_7H_{14}	Ethylcyclopentane	Cycloparaffin	103·5	$C_{10}H_{12}$	5,6,7,8-Tetrahydronaphthalene	Aromatic-cycloparaffin	207·6
C_8H_{16}	1,1,3-Trimethylcyclopentane	Cycloparaffin	104·9				
C_8H_{18}	2,2-Dimethylhexane	Paraffin	106·8	$C_{11}H_{16}$	Alkylbenzene*	Aromatic	208·5
C_7H_8	Toluene	Aromatic	110·6	$C_{11}H_{16}$	Alkylbenzene*	Aromatic	212·3
C_8H_{18}	2-Methylheptane	Paraffin	117·6	$C_{12}H_{26}$	*n*-Dodecane	Paraffin	216·3
C_8H_{16}	*cis*-1,3-Dimethylcyclohexane	Cycloparaffin	120·1	$C_{10}H_8$	Naphthalene	Aromatic	218·0
C_8H_{16}	*trans*-1,2-Dimethylcyclohexane*	Cycloparaffin	123·4	$C_{12}H_{16}$	Phenylcyclopentane*	Aromatic-cycloparaffin	220·7
C_8H_{18}	*n*-Octane	Paraffin	125·7				
C_8H_{16}	Ethylcyclohexane	Cycloparaffin	131·8	$C_{11}H_{14}$	2-Methyl-5,6,7,8-tetrahydronaphthalene	Aromatic-cycloparaffin	229·0
C_9H_{20}	2,6-Dimethylheptane	Paraffin	135·2				
C_8H_{10}	Ethylbenzene	Aromatic	136·2	$C_{11}H_{14}$	1-Methyl-5,6,7,8-tetrahydronaphthalene	Aromatic-cycloparaffin	234·4
C_9H_{18}	1,1,3-Trimethylcyclohexane	Cycloparaffin	136·7				
C_8H_{10}	*p*-Xylene	Aromatic	138·4	$C_{11}H_{10}$	2-Methylnaphthalene	Aromatic	241·1
C_8H_{10}	*m*-Xylene	Aromatic	139·1	$C_{11}H_{10}$	1-Methylnaphthalene	Aromatic	244·8
C_9H_{20}	2,3-Dimethylheptane	Paraffin	140·5				

* Identity not definitely established.

† Identity not yet determined.

The above crude petroleum which was selected for the systematic exhaustive investigation was classed as 'intermediate' in composition. The Engler distillation of the original crude was given by the Marland Oil Company as follows: naphtha, 38·9%; kerosine, 15·4%; gas oil, 16·0%; wax distillate, 18·1%; bottoms, 10·2%. A report of the standard U.S. Bureau of Mines Hempel distillation, given in reference [66], gave the following results: light gasoline, 12·4%; naphtha, 30·0%; kerosine, 12·7%; gas oil, 16·6%; lubricating distillate, 14·3%; residuum, 12·5%. A 600-gal. lot of this material was first distilled in a semi-commercial column by the Sun Oil Company, and the fractions were sent to the National Bureau of Standards.

XIII. Hydrocarbons in the Gas, Gasoline, and Kerosine Fractions of the Oklahoma Petroleum

In Table III are listed the 72 hydrocarbon compounds that have been separated from the Ponca, Oklahoma, petroleum as of 31 December 1946, using appropriate combinations of the several fractionating processes in proper sequence [101].

These hydrocarbons are distributed according to type and boiling range as shown in Table IV.

XIV. Separation of the Lubricant Fraction of the Oklahoma Petroleum

Because of the greater complexity of the lubricant fraction, and of the lack of sufficient quantity of material, the resolution of the lubricant fraction of the Ponca, Oklahoma, petroleum under investigation was carried to the

TABLE IV

Distribution, by Type and Boiling Range, of the Hydrocarbons separated from the Ponca, Oklahoma, Petroleum by the A.P.I. Research Project 6 as of 31 December 1946

Type	*Gas*	*Gasoline*	*Kerosine*	*Total*
Normal paraffins . . .	4	6	1	11
Isoparaffins	1	17	0	18
Alkylcyclopentanes . . .	..	7	..	7
Alkylcyclohexanes* . . .	..	9*	..	9*
Bicycloparaffins . . .	..	1	..	1
Alkylbenzenes . . .	..	14	5	19
Alkylnaphthalenes . . .	..	..	3	3
Bicyclo-aromatic-naphthene .	..	..	4	4
Total	5	54	13	72

* One of these compounds may be an alkylcyclopentane.

stage of 'homogeneous' fractions, each containing molecules of the same size and type.

Fig. 24 illustrates the scheme of separating the lubricant fraction into four broad portions having quite different properties. The material was dewaxed at −18° C. with ethylene chloride to produce a 'wax' portion containing, in addition to the true wax, a considerable portion of clear oil. The remaining material was then subjected to extraction at about 40° C. with liquid sulphur dioxide to produce a 'sulphur-dioxide extract'. The material insoluble in the sulphur dioxide was treated by adsorption with silica gel to produce a 'water-white' oil and a portion representing the 'silica-gel hold-up'. The 'sulphur-dioxide extract' was brought into solution in liquid sulphur dioxide at −55° C., and extracted with petroleum ether at the same temperature to produce a 'petroleum-ether-soluble' portion and an 'asphaltic' portion, the latter from the material remaining in the sulphur dioxide layer. The 'petroleum-ether-soluble' material was combined with the 'silica-gel hold-up' to make what may be called the 'extract' portion of the lubricant fraction. In this manner the original lubricant fraction was separated into the following four broad fractions: 'wax' portion, 35%; 'asphaltic' portion, 8%; 'extract' portion, 22%; 'water-white' oil portion, 35%.

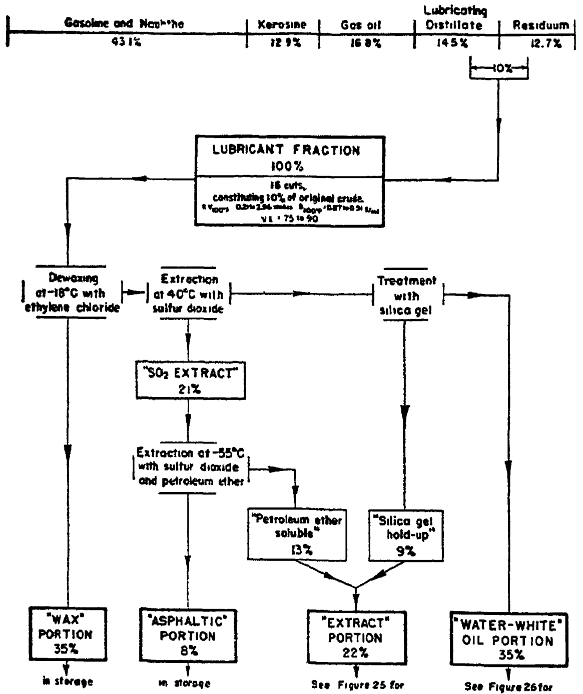

Gasoline and Naphtha
43.1%
Kerosine
12.9%
Gas oil
16.8%
Lubricating Distillate
14.5%
Residuum
12.7%
10%
LUBRICANT FRACTION
100%
16 cuts,
constituting 10% of original crude.
VI = 75 to 90
Dewaxing at −18°C with ethylene chloride
Extraction at 40°C with sulfur dioxide
Treatment with silica gel
"SO₂ EXTRACT"
21%
Extraction at −55°C with sulfur dioxide and petroleum ether
"Petroleum ether soluble"
13%
"Silica gel hold-up"
9%
"WAX" PORTION
35%
in storage
"ASPHALTIC" PORTION
8%
in storage
"EXTRACT" PORTION
22%
See Figure 25 for further separation
"WATER-WHITE" OIL PORTION
35%
See Figure 26 for further separation

FIG. 24. Chart showing the separation of the lubricant fraction into four broad portions.

The so-called 'wax' portion (which contains a considerable amount of clear oil in addition to the true wax) and the 'asphaltic' portion (the greater part of which was solid at room temperature, and which contains all the black tar-like constituents) were placed in storage and were not further separated. The 'extract' portion and the 'water-white' oil portion were each subjected to an exhaustive separation with respect both to size and type of molecules.

Fig. 25 illustrates the manner in which the 'water-white' oil portion was fractionated exhaustively by distillation and extraction. This oil was first subjected to a systematic distillation in high vacuum, through about eight stages, to produce a large number of substantially constant-boiling fractions. An indication of the properties of these fractions, which are mixtures of different types of molecules, is given in the two blocks, one at the low-boiling and one at the high-boiling end. These substantially constant-boiling fractions were then subjected to extraction with reflux in 46-ft. columns, with acetone (plus some water for the more soluble fractions) as the solvent, to produce the final fractions shown in the lower part of the figure. The nature of these final fractions is indicated by the properties given in the blocks for the most soluble and the least soluble fractions of both the low-boiling and the high-boiling ends, together with one fraction in the centre of the 'spread' formation.

Fig. 26 illustrates the exhaustive separation of the 'extract' portion, by distillation and extraction. This material was processed in the same manner as was the 'water-white' oil, except that the extraction occurred in 55-ft. columns with methyl cyanide (plus some acetone for the less soluble fractions) as the solvent. The nature of the final fractions is indicated by the properties in the blocks.

The quantity of each of the final 'homogeneous' fractions of both the 'water-white' oil and 'extract' portions was about 15 g., representing 1/40,000th part of the original crude petroleum from which it came, and consisted of compounds of substantially similar sizes and types. These fractions, although far from being pure compounds, appear to be nearer to pure compounds than any material (except normal paraffin hydrocarbons) hitherto separated from the lubricant fraction of any crude petroleum.

Both the 'wax' and 'water-white' oil portions of this lubricant fraction were substantially pure hydrocarbon material. The 'extract' portion contained some sulphur, nitrogen, and oxygen compounds, but the bulk of the non-hydrocarbon material remained in the 'asphaltic' portion. Analyses of the 'extract' portion showed that the fractions of the distillate (see row in the upper part of Fig. 26) contained on the average about 0·9% sulphur, 0·1% nitrogen, and 0·5% oxygen. The final process of extraction distributed this non-hydrocarbon material among the various final homogeneous fractions as shown in the blocks in the lower part of Fig. 26 and as illustrated in Fig. 27. Details of the experimental apparatus and procedures for separating the lubricant fraction have been reported [43, 45, 48, 51, 63, 64].

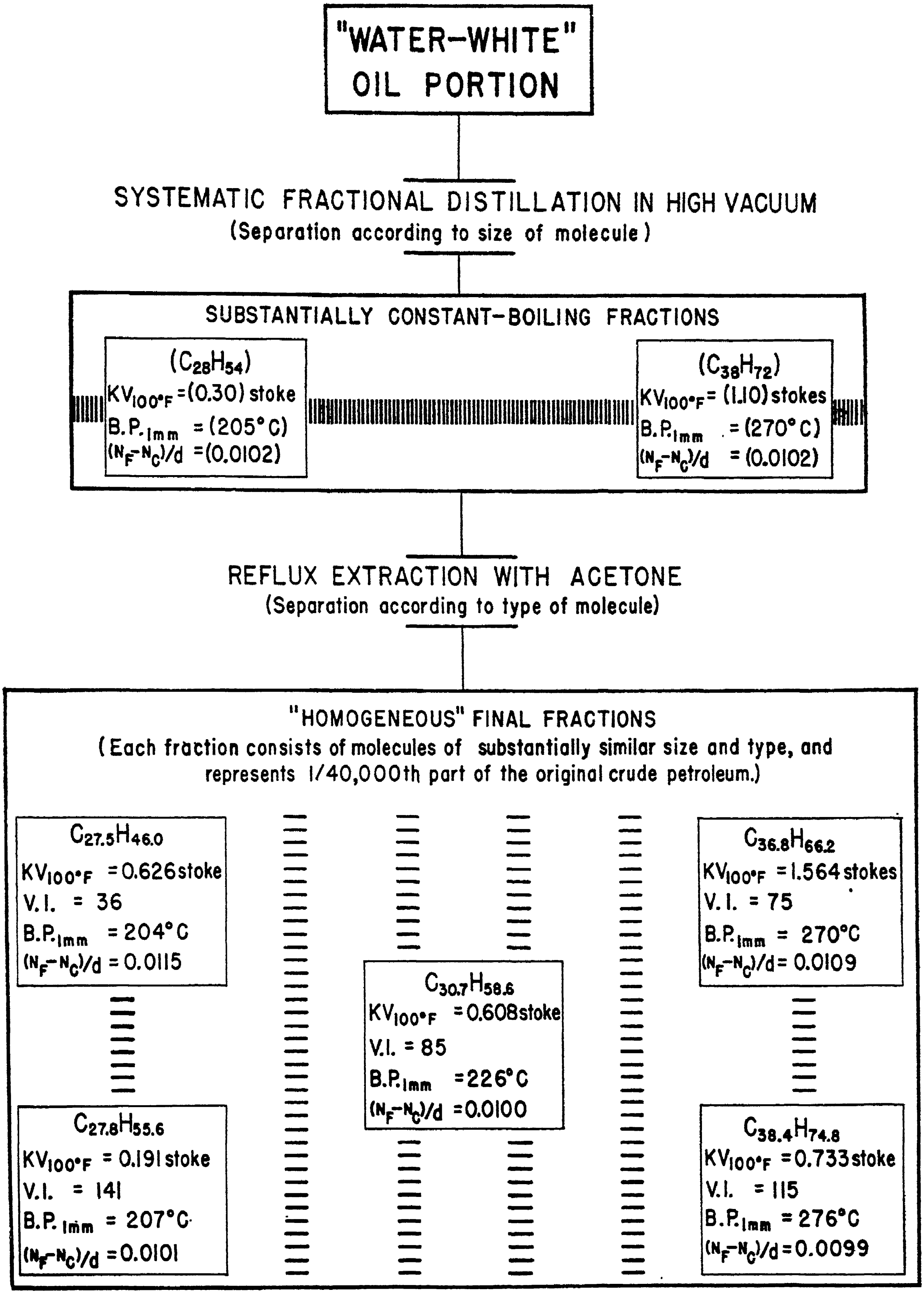

"WATER-WHITE" OIL PORTION
SYSTEMATIC FRACTIONAL DISTILLATION IN HIGH VACUUM
(Separation according to size of molecule)
SUBSTANTIALLY CONSTANT-BOILING FRACTIONS
($C_{28}H_{54}$)
$KV_{100°F}$ = (0.30) stoke
$B.P._{1mm}$ = (205° C)
$(N_F-N_C)/d$ = (0.0102)
($C_{38}H_{72}$)
$KV_{100°F}$ = (1.10) stokes
$B.P._{1mm}$ = (270° C)
$(N_F-N_C)/d$ = (0.0102)
REFLUX EXTRACTION WITH ACETONE
(Separation according to type of molecule)
"HOMOGENEOUS" FINAL FRACTIONS
(Each fraction consists of molecules of substantially similar size and type, and represents 1/40,000th part of the original crude petroleum.)
$C_{27.5}H_{46.0}$
$KV_{100°F}$ = 0.626 stoke
V.I. = 36
$B.P._{1mm}$ = 204°C
$(N_F-N_C)/d$ = 0.0115
$C_{36.8}H_{66.2}$
$KV_{100°F}$ = 1.564 stokes
V.I. = 75
$B.P._{1mm}$ = 270°C
$(N_F-N_C)/d$ = 0.0109
$C_{30.7}H_{58.6}$
$KV_{100°F}$ = 0.608 stoke
V.I. = 85
$B.P._{1mm}$ = 226°C
$(N_F-N_C)/d$ = 0.0100
$C_{27.8}H_{55.6}$
$KV_{100°F}$ = 0.191 stoke
V.I. = 141
$B.P._{1mm}$ = 207°C
$(N_F-N_C)/d$ = 0.0101
$C_{38.4}H_{74.8}$
$KV_{100°F}$ = 0.733 stoke
V.I. = 115
$B.P._{1mm}$ = 276°C
$(N_F-N_C)/d$ = 0.0099

FIG. 25. Chart showing the exhaustive separation of the 'water-white' oil portion of the lubricant fraction.

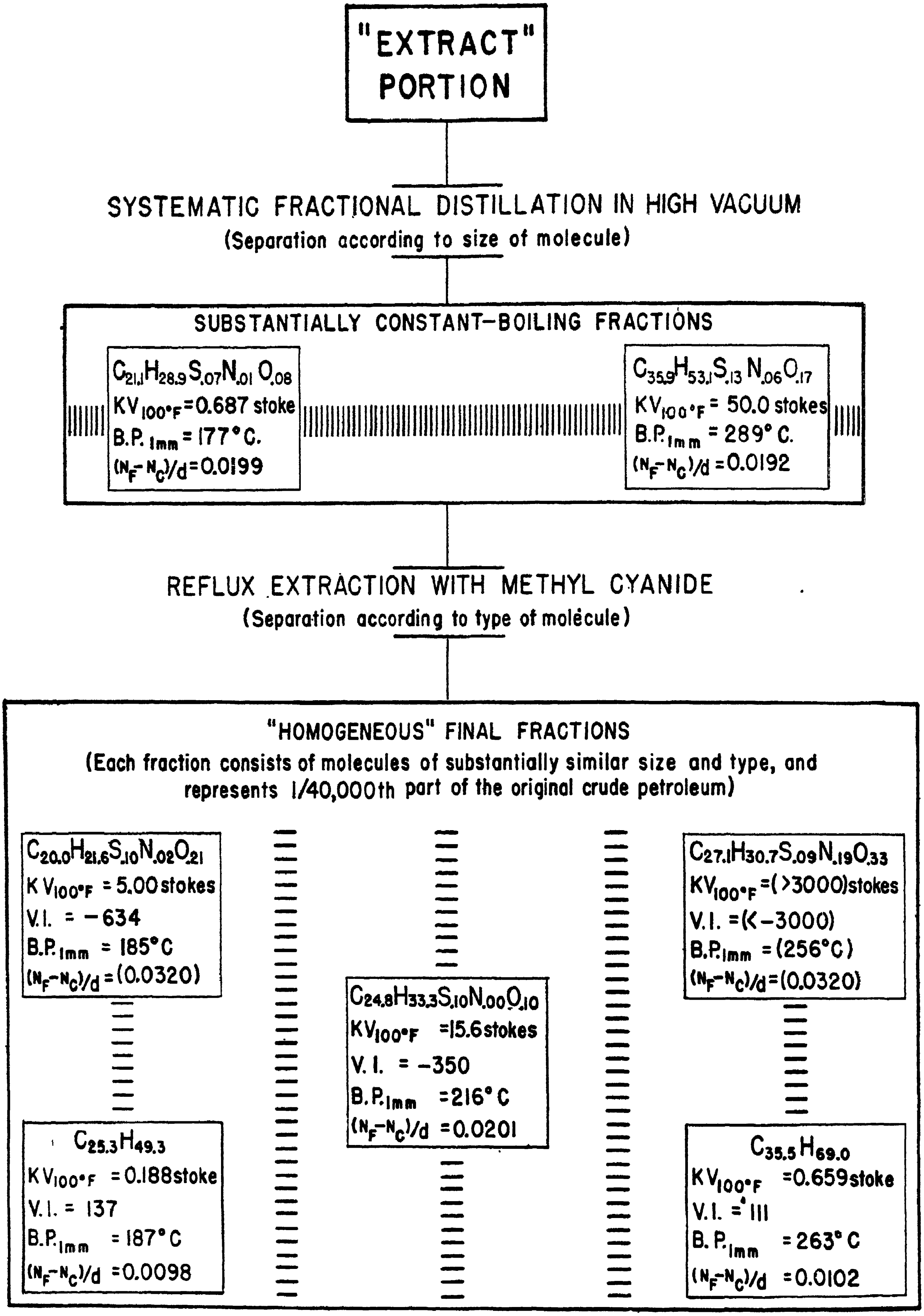

"EXTRACT" PORTION
SYSTEMATIC FRACTIONAL DISTILLATION IN HIGH VACUUM
(Separation according to size of molecule)
SUBSTANTIALLY CONSTANT-BOILING FRACTIONS
$C_{21.1}H_{28.9}S_{.07}N_{.01}O_{.08}$
$KV_{100°F}$ = 0.687 stoke
$B.P._{1mm}$ = 177° C.
$(N_F-N_C)/d$ = 0.0199
$C_{35.9}H_{53.1}S_{.13}N_{.06}O_{.17}$
$KV_{100°F}$ = 50.0 stokes
$B.P._{1mm}$ = 289° C.
$(N_F-N_C)/d$ = 0.0192
REFLUX EXTRACTION WITH METHYL CYANIDE
(Separation according to type of molecule)
"HOMOGENEOUS" FINAL FRACTIONS
(Each fraction consists of molecules of substantially similar size and type, and represents 1/40,000th part of the original crude petroleum)
$C_{20.0}H_{21.6}S_{.10}N_{.02}O_{.21}$
$KV_{100°F}$ = 5.00 stokes
V.I. = −634
$B.P._{1mm}$ = 185°C
$(N_F-N_C)/d$ = (0.0320)
$C_{25.3}H_{49.3}$
$KV_{100°F}$ = 0.188 stoke
V.I. = 137
$B.P._{1mm}$ = 187°C
$(N_F-N_C)/d$ = 0.0098
$C_{24.8}H_{33.3}S_{.10}N_{.00}O_{.10}$
$KV_{100°F}$ = 15.6 stokes
V.I. = −350
$B.P._{1mm}$ = 216°C
$(N_F-N_C)/d$ = 0.0201
$C_{27.1}H_{30.7}S_{.09}N_{.19}O_{.33}$
$KV_{100°F}$ = (>3000) stokes
V.I. = (<−3000)
$B.P._{1mm}$ = (256°C)
$(N_F-N_C)/d$ = (0.0320)
$C_{35.5}H_{69.0}$
$KV_{100°F}$ = 0.659 stoke
V.I. = 111
$B.P._{1mm}$ = 263°C
$(N_F-N_C)/d$ = 0.0102

FIG. 26. Chart showing the exhaustive separation of the 'extract' portion of the lubricant fraction.

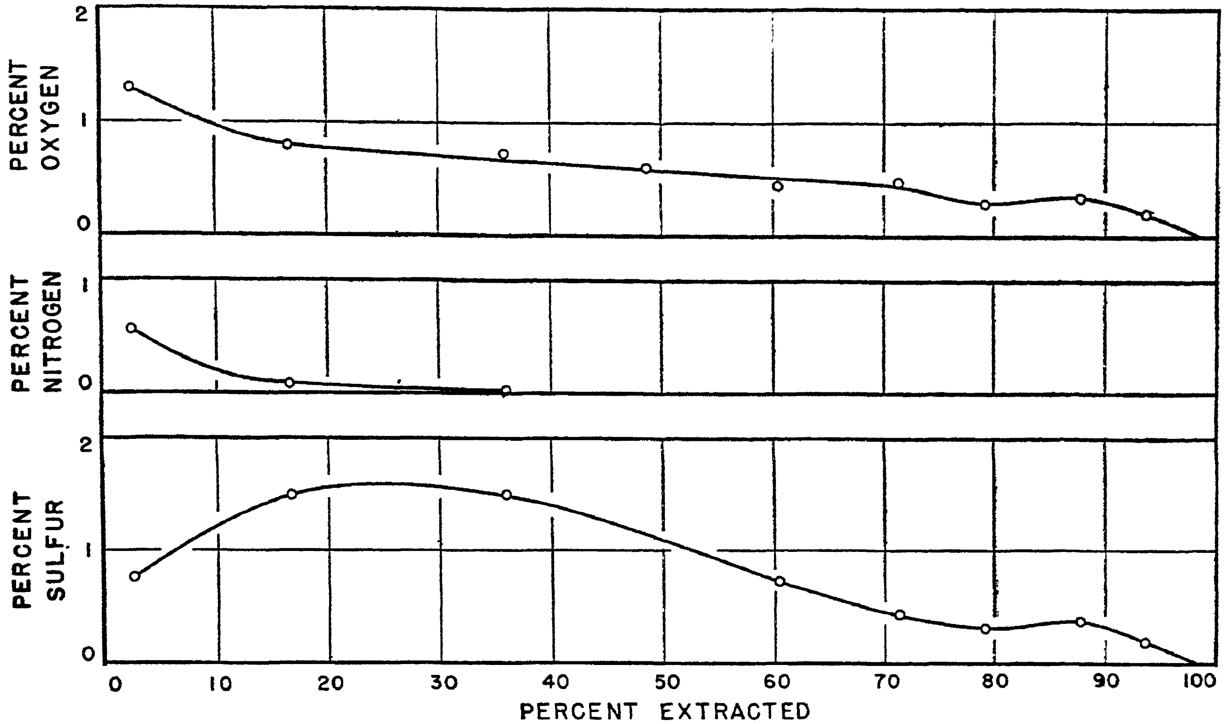


FIG. 27. Chart showing the content of sulfur, nitrogen, and oxygen in one series of final homogeneous fractions of the 'extract' portion of the lubricant fraction.

The scale of ordinates gives the percentage by weight of sulfur, nitrogen, and oxygen. The scale of abscissae gives the percentage extracted of the substantially constant-boiling fraction (see center column of the lower part of Fig. 26).

XV. Types of Hydrocarbons in the Lubricant Fraction of the Oklahoma Petroleum

The following properties were determined for all the important final fractions from both the 'water-white' oil and 'extract' portions: molecular weight; content of carbon and hydrogen; content of sulphur, nitrogen, and oxygen; boiling-point at a pressure of 1 mm. Hg; density; refractive index, N_D; refractive dispersion, N_F–N_C; kinematic viscosity at 100° and 210° F.; and aniline point. The aromatic content of selected fractions of the 'extract' portion was determined by hydrogenation. The foregoing properties were also determined for the hydrogenated material.

These data on the properties of the fractions of the 'water-white' oil and 'extract' portions were compared with those of known hydrocarbons of high molecular weight in order to deduce the kinds of molecules constituting the various fractions. From these correlations, the information displayed in Figs. 28 and 29 and in Table V was obtained.

TABLE V

Approximate Average Analysis of the Middle Part of the Lubricant Fraction with respect to Kinds of Molecules

(These molecules contain from 25 to 35 carbon atoms)

Portion	*Percentage of lubricant fraction*	*Molecules composed of the following component parts with the rings condensed (that is, joined through two carbon atoms) when more than one:*	*Percentage of the given portion‡*	*Percentage of lubricant fraction‡*
'Water-white' oil	35	1 naphthene* ring +paraffin groups	92 (15)	32·2 (5·3)
		2 naphthene rings +paraffin groups	(45)	(15·7)
		3 naphthene rings +paraffin groups	(32)	(11·2)
		1 naphthene ring +1 aromatic ring +paraffin groups	8	2·8
		2 naphthene rings+1 aromatic ring +paraffin groups		
'Extract'†	22	2 naphthene rings +paraffin groups	8	1·8
		3 naphthene rings +paraffin groups		
		2 naphthene rings+1 aromatic ring +paraffin groups	25	5·5
		3 naphthene rings+1 aromatic ring +paraffin groups		
		2 naphthene rings+2 aromatic rings+paraffin groups	67 (37)	14·7 (8·1)
		1 naphthene ring +3 aromatic rings+paraffin groups	(30)	(6·6)
'Wax'	35	Normal paraffins (plus possibly some isoparaffins)	50 to 75	18 to 26
		1, 2, or 3 naphthene rings +paraffin groups	50 to 25	17 to 9
'Asphaltic'	8	Probably highly condensed multi-ring aromatics, very low in hydrogen, together with the bulk of the non-hydrocarbon material		

* Cycloparaffin. † Contains some non-hydrocarbon material.

‡ The values in parenthesis are less reliable than the others.

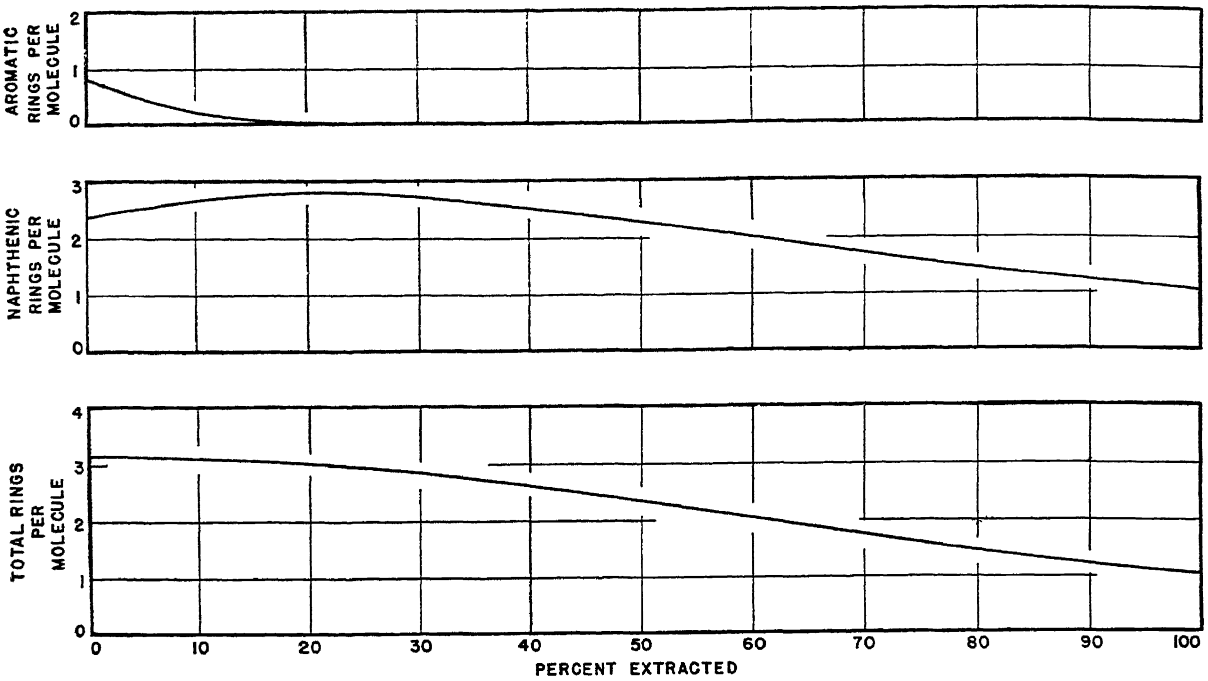


Fig. 28. Chart showing the number of rings per molecule for one series of homogeneous fractions of the 'water-white' oil portion of the lubricant fraction.

The scale of ordinates gives, per molecule, the total number of rings, the number of naphthene or cycloparaffin rings, and the number of aromatic rings. The scale of abscissae gives the percentage extracted of the substantially constant-boiling fraction.

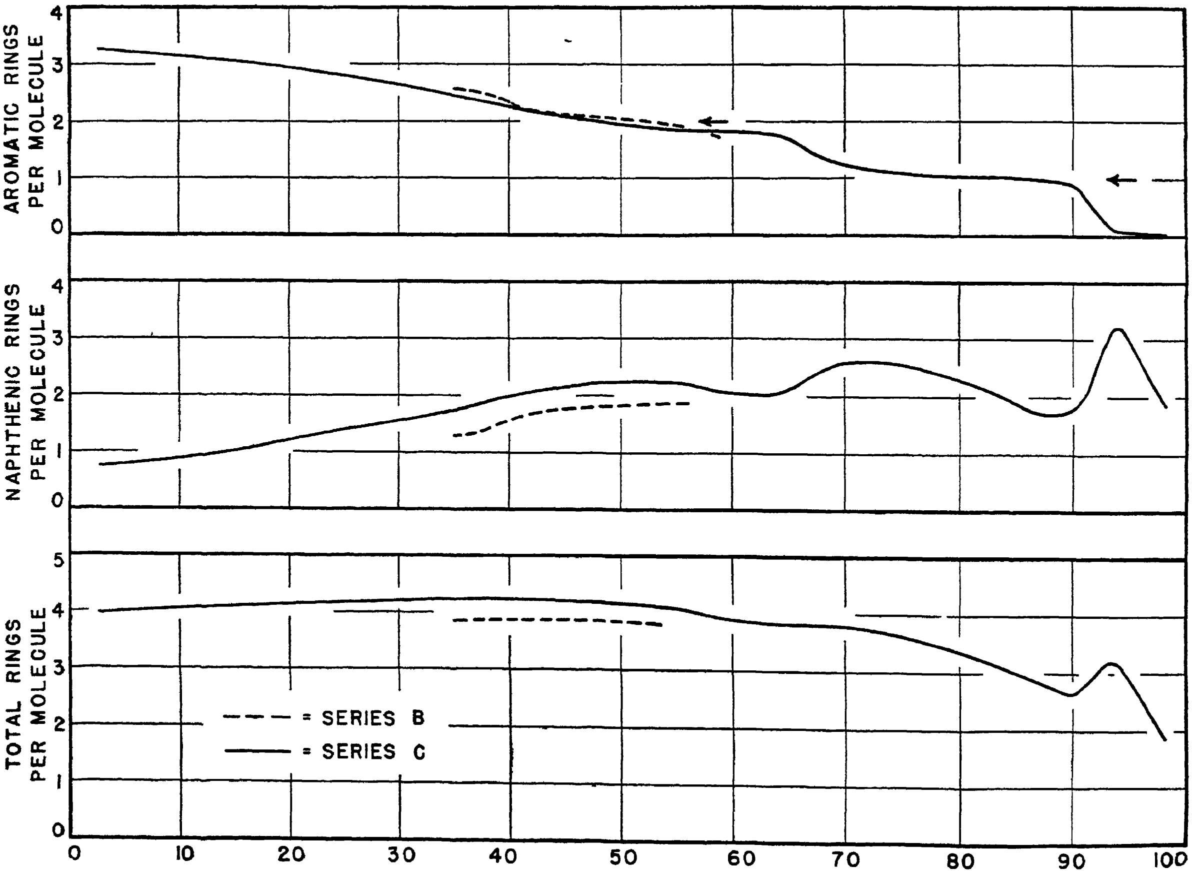


Fig. 29. Chart showing the number of rings per molecule for one series (and part of another) of homogeneous fractions of the 'extract' portion of the lubricant fraction.

The scale of ordinates gives, per molecule, the total number of rings, the number of naphthene or cycloparaffin rings, and the number of aromatic rings. The scale of abscissae gives the percentage extracted of the substantially constant-boiling fraction.

From the data obtained, the following average analysis was deduced with regard to the kinds of hydrocarbons in the middle portion of the original lubricant fraction of this Oklahoma petroleum:

(*a*) Normal paraffins (plus possibly a small amount of isoparaffins), 18 to 26%.

(*b*) Naphthenes or cycloparaffins, with one, two, or three cycloparaffin rings and paraffin side chains, 51 to 43%.

(*c*) Mixed cycloparaffin-aromatic hydrocarbons with one aromatic ring and, in the same molecule, one, two, or three cycloparaffin rings, 8·3%.

(*d*) Mixed cycloparaffin-aromatic hydrocarbons with two aromatic rings (condensed as in naphthalene) and, in the same molecule, two cycloparaffin rings, 8·1%.

(*e*) Mixed cycloparaffin-aromatic hydrocarbons with three aromatic rings (condensed) and, in the same molecule, one cycloparaffin ring, 6·6%.

(*f*) 'Asphaltic' constituents, 8%.

The striking part of this analysis is the absence of any significant amount of purely isoparaffin hydrocarbons and, except in the 'asphaltic' portion, of any purely aromatic hydrocarbons.

Complete details of the above have been reported [45, 49, 51, 65, 66].

XVI. Hydrocarbons in the Gasoline Fraction of Seven Representative Crudes

The results obtained from the exhaustive fractionation of the large quantity of the Ponca, Oklahoma, petroleum serve to indicate what hydrocarbon compounds are in petroleum and the amounts of them which may be expected to be present in a petroleum of intermediate type. The next point of interest is how the amounts of the hydrocarbon components vary in petroleums of appreciably different type. In order to obtain some information along these lines, the project began an investigation of the hydrocarbons in the gasoline fraction of seven representative crudes [81, 83, 108].

The Advisory Committee for the A.P.I. Research Project 6 drew up the following specifications for the naphthas to be investigated.

The gasoline fraction should be the straight-run cut, preferably from large-scale operation or at least obtained by fractionation comparable to refinery fractionation. The 90% point should be near 350° F. (177° C.). The material should be washed with caustic to remove hydrogen sulphide. The sample should contain its full proportion of hexanes but should preferably be debutanized. Each contributor should provide 15 gal. of the product, of which 5 gal. should be sent to Project 6 at the National Bureau of Standards and 10 gal. should be retained in safe storage by the supplier.

The seven naphthas selected by the Advisory Committee for investigation are shown in Table VI, which gives the field from which the crude was produced, the general type of the naphtha, and the company supplying the sample. As may be seen from the table, the naphthas include two which are classed as intermediate, one high in paraffins, one high in normal paraffins, one high in isoparaffins, one high in naphthenes, and one high in aromatics. The intermediate naphtha labelled Ponca, Okla. is from the original Mid-Continent petroleum that was under investigation by the A.P.I. Research Project 6 for many years and from which a total of 72 pure hydrocarbons have been isolated from the gas, gasoline, and kerosine fractions, as of 31 December 1946 [101].

TABLE VI

Source and General Type of the Naphthas investigated

Field	*Type*	*Supplier*
Ponca, Okla. . .	Intermediate	Continental Oil Co.
East Texas . .	"	Standard Oil Development Co.
Bradford, Pa. . .	High in paraffins	Quaker State Oil Refining Co.
Greendale-Kawkawlin, Mich. . . .	High in normal paraffins	Pure Oil Co.
Winkler, Tex. . .	High in isoparaffins	Standard Oil Co. (Indiana).
Midway, Calif. . .	High in naphthenes	Standard Oil Co. of California
Conroe, Texas . .	High in aromatics	Humble Oil and Refining Co.

The method of analysis consisted essentially in applying the processes of adsorption and distillation to the naphtha fraction. The process of adsorption, with silica gel as the adsorbent, was used to separate the naphtha fraction into two portions, one containing all the paraffin and naphthene hydrocarbons, and the other containing all the aromatic hydrocarbons together with the non-hydrocarbon components (principally sulphur compounds). From the latter portion, the small amount of non-hydrocarbon components was separated by further adsorption to give a clean aromatic portion. Then the paraffin-naphthene portion and the clean aromatic portions were separately subjected to an analytical distillation at high reflux ratio in columns of high separating efficiency and low hold-up.

It is well known that a mixture of aromatic hydrocarbons with paraffins and naphthenes constitutes a non-ideal mixture, and that the distillation of such a mixture yields quite unsatisfactory results, primarily because aromatic hydrocarbons in mixtures with paraffins and naphthenes have much greater partial pressures at a given temperature and concentration than are called for by the ideal solution laws, and hence always concentrate in the distillate at temperatures appreciably below their normal boiling-points. On the other hand, a mixture of paraffins and naphthenes (cycloparaffins) is substantially ideal, and likewise a mixture of aromatic hydrocarbons is substantially ideal. The separate distillation of these two mixtures yields results which are quite satisfactory. This is a great advantage of the present method used for these analyses.

Table VII gives the amounts of the aromatic and sulphur compounds in the naphthas as received.

TABLE VII

Aromatic and Sulphur Content of Naphthas as received

Naphtha	*Sulphur content*	*Sulphur compounds content*	*Aromatic hydrocarbons content*
	% (*by wt.*)	% (*by vol.*)	% (*by vol.*)
Ponca, Okla. . . .	0·017	0·06±0·03	9·8±0·2
East Texas . . .	0·033	0·12±0·04	10·4±0·2
Bradford, Pa. . .	0·012	0·04±0·02	8·3±0·3
Greendale-Kawkawlin, Mich. . . .	0·014	0·05±0·02	7·2±0·2
Winkler, Tex. . .	0·159	0·59±0·10	4·9±0·2
Midway, Calif. . .	0·045	0·17±0·05	8·0±0·2
Conroe, Tex. . . .	0·002	0·007±0·005	27·6±0·5

For the Ponca, Oklahoma, naphtha, Fig. 30 gives for the aromatic portion plots of the boiling-point and the refractive index of the distillate as a function of its volume. Similar plots have been reported for the other six naphthas.

Table VIII shows that the paraffin-naphthene portions of the seven naphthas contain the same hydrocarbon components, the difference between the several naphthas being in the relative amounts of the components.

Table IX gives in the second and third columns the relative amounts of total paraffins and total naphthenes in the paraffin-naphthene portion, 40° to 102° C., for the seven naphthas. In the last four columns of Table IX are given the relative amounts of the normal paraffins, isoparaffins, alkyl cyclopentanes, and alkyl cyclohexanes, which four classes appear (as will be seen later) to be the ones which are characteristic of the paraffin-naphthene portion of several crudes. It is interesting to note the large range in composition covered: Total paraffins, 31 to 76; total naphthenes, 24 to 69; normal paraffins, 9 to 63; isoparaffins, 13 to 62; alkyl cyclopentanes, 8 to 41; alkyl cyclohexanes, 16 to 44.

Figure 31 gives a triangular plot which shows graphically the relative amounts of the normal paraffins, isoparaffins, and total naphthenes. These data indicate the extreme over-all range in composition of the non-aromatic portion of the seven naphthas.

Table X gives, for each of the seven naphthas, the relative amounts of the following individual components and groups of components:

C_6 and C_7 normal paraffins.
C_6 and C_7 isoparaffins.
C_6 isoparaffins.
Individual C_6 isoparaffins.

TABLE VIII

Amounts of the Individual Hydrocarbons in the Paraffin-Naphthene Portion, 40° to 102° C., of the seven Naphthas

Component	*Boiling-point at 1 atm.*	*Ponca, Okla.*	*East Texas*	*Bradford, Pa.*	*Greendale-Kawkawlin, Mich.*	*Winkler, Tex.*	*Midway, Calif.*	*Conroe, Tex.*	*Estimated uncertainty of individual determination*
		Percentage, by volume, of the paraffin-naphthene portion, 40° to 102° C.							
	°C.								±
Cyclopentane	49·26	0·40	0·74	0·57	0·62	1·16	2·39	0·76	0·12
2,2-Dimethylbutane	49·74	0·33	0·44	0·40	0·13	0·92	0·81	0·61	0·12
2,3-Dimethylbutane	57·99	0·66	1·09	1·14	0·76	2·08	0·98	0·99	0·12
2-Methylpentane	60·27	3·27	6·30	9·10	3·45	6·61	5·50	4·94	0·12
3-Methylpentane	63·28	3·03	4·79	5·41	2·27	16·53	3·73	3·42	0·12
n-Hexane	68·74	15·79	12·59	15·61	29·06	4·47	6·14	7·59	0·10
Methylcyclopentane	71·81	7·60	9·49	3·65	4·04	6·12	13·02	9·11	0·10
2,2-Dimethylpentane	79·20	0·83	2·38	2·29	0·76	3·25	1·47	1·29	0·20
2,4-Dimethylpentane	80·51								
Cyclohexane	80·74	6·23	4·80	4·75	5·14	2·57	8·10	13·29	0·15
1,1-Dimethylcyclopentane	87·5	1·42	1·43	1·41	0·93	2·45	1·87	1·37	0·40
2,3-Dimethylpentane	89·79	9·46	9·23	9·76	4·86	17·67	7·01	7·60	0·50
2-Methylhexane	90·05								
trans-1,3-Dimethylcyclopentane	90·8	10·41	10·23	4·00	1·76	6·08	17·05	4·77	0·60
trans-1,2-Dimethylcyclopentane	91·9	3·56	4·11	3·76	0·63	4·69	6·66	1·25	0·50
3-Methylhexane	91·95	2·87	3·05	4·03	0·93	14·55	1·96	1·43	0·50
n-Heptane	98·43	19·92	12·13	18·82	34·04	5·02	3·85	10·63	0·12
Methylcyclohexane	100·93	14·22	17·20	15·30	10·61	5·82	19·46	30·95	0·20
Total	..	100·00	100·00	100·00	100·00	100·00	100·00	100·00	..

TABLE IX

Relative Amounts of the Total Paraffins and Total Naphthenes, and of Normal Paraffins, Isoparaffins, Alkyl Cyclopentanes, and Alkyl Cyclohexanes

Naphtha	*Percentage, by volume, of the paraffin-naphthene portion, 40° to 102° C.*					
	Total paraffins	*Total naphthenes*	*Normal paraffins*	*Iso-paraffins*	*Alkyl cyclo-pentanes*	*Alkyl cyclo-hexanes*
Ponca, Okla.	56·2	43·8	35·7	20·5	23·4	20·4
East Texas	52·0	48·0	24·7	27·3	26·0	22·0
Bradford, Pa.	66·6	33·4	34·4	32·2	13·4	20·0
Greendale-Kawkawlin, Mich.	76·3	23·7	63·1	13·2	8·0	15·7
Winkler, Texas	71·1	28·9	9·5	61·6	8·4	20·5
Midway, Calif.	31·5	68·5	10·0	21·5	41·0	27·5
Conroe, Texas	38·5	61·5	18·2	20·3	17·3	44·2

TABLE X

Relative Amounts of the Components within the Various Groups

Group	*Components*	*Boiling-point at 1 atm.* ° C.	*Ponca, Okla.*	*East Texas*	*Brad-ford, Pa.*	*Green-dale-Kaw-kawlin, Mich.*	*Wink-ler, Tex.*	*Mid-way, Calif.*	*Con-roe, Tex.*	*Range of values*	*Aver-age value*
Normal paraffins .	*n*-Hexane	68·74	44	51	45	46	47	61	42	42 to 61	48
	n-Heptane	98·43	56	49	55	54	53	39	58	39 to 58	52
	Total	..	100	100	100	100	100	100	100	..	100
Isoparaffins . .	C_6	..	36	46	50	50	43	51	49	35 to 51	47
	C_7	..	64	54	50	50	57	49	51	49 to 64	53
	Total	..	100	100	100	100	100	100	100	..	100
C_6 isoparaffins .	Dimethylbutanes	..	14	13	10	14	12	16	16	10 to 16	14
	Methylpentanes	..	86	87	90	86	88	84	84	84 to 90	86
	Total	..	100	100	100	100	100	100	100	..	100
Individual C_6 iso-paraffins . .	2,2-Dimethylbutane	49·74	5	4	3	2	4	7	6	2 to 7	4
	2,3-Dimethylbutane	57·99	9	9	7	12	8	9	10	7 to 12	9
	2-Methylpentane	60·27	45	50	56	52	25	50	50	25 to 56	47
	3-Methylpentane	63·28	41	37	34	34	63	34	34	34 to 63	40
	Total	..	100	100	100	100	100	100	100	..	100
Individual C_7 iso-paraffins . .	2,2-Dimethylpentane	79·20	6	16	14	12	9	14	12	6 to 16	12
	2,4-Dimethylpentane	80·51									
	2,3-Dimethylpentane	89·79	72	63	61	74	50	67	74	50 to 74	66
	2-Methylhexane	90·05									
	3-Methylhexane	91·95	22	21	25	14	41	19	14	14 to 41	22
	Total	..	100	100	100	100	100	100	100	..	100
Alkyl cyclopentanes	C_5	..	2	3	4	8	6	6	4	2 to 8	5
	C_6	..	32	36	27	50	30	32	53	27 to 53	37
	C_7	..	66	61	69	42	64	62	43	41 to 68	58
	Total	..	100	100	100	100	100	100	100	..	100
Individual alkyl cyclopentanes .	Cyclopentane	49·26	2	3	4	8	6	6	4	2 to 8	5
	Methylcyclopentane	71·81	32	36	27	50	30	32	53	27 to 53	37
	1,1-Dimethylcyclopentane	87·5	6	6	11	12	12	5	8	5 to 12	9
	trans-1,3-Dimethylcyclopentane	90·8	45	39	30	22	29	41	28	22 to 45	33
	trans-1,2-Dimethylcyclopentane	91·9	15	16	28	8	23	16	7	7 to 28	16
	Total	..	100	100	100	100	100	100	100	..	100
Individual alkyl cyclohexanes .	Cyclohexane	80·74	30	21	24	33	31	29	30	21 to 33	28
	Methylcyclohexane	100·93	70	79	76	67	69	71	70	67 to 79	72
	Total	..	100	100	100	100	100	100	100	..	100
Aromatics . .	C_6	..	9	4	4	13	10	5	6	4 to 13	7
	C_7	..	30	29	31	37	20	30	38	20 to 38	31
	C_8	..	61	67	65	50	70	65	56	50 to 70	62
	Total	..	100	100	100	100	100	100	100	..	100
Individual C_8 aro-matics . .	Ethylbenzene	136·19	18	17	9	15	25	24	8	8 to 25	17
	p-Xylene	138·35	9	13	16	12	39	16	16	9 to 39	17
	m-Xylene	139·11	48	48	56	51	26	38	57	26 to 57	46
	o-Xylene	144·42	25	22	19	22	10	22	19	10 to 25	20
	Total	..	100	100	100	100	100	100	100	..	100

Individual C_7 isoparaffins.
C_5, C_6, and C_7 alkyl cyclopentanes, 40° to 102° C.
Individual alkyl cyclopentanes, 40° to 102° C.
C_6 and C_7 alkyl cyclohexanes.
C_6, C_7, and C_8 aromatic hydrocarbons.
Individual C_8 aromatic hydrocarbons.

For each of these groups there are given the averages of the relative amounts of the components, together with the ranges covered. It is seen that, within the given classes, the individual hydrocarbons occur in proportions which are of the same order of magnitude for the seven naphthas.

Table XI

Relative Amounts of the Alkyl Cyclopentanes and Alkyl Cyclohexanes in the Seven Naphthas, 40° to 102° C.

Components	*Ponca, Okla.*	*East Texas*	*Bradford, Pa.*	*Green-dale-Kawkawlin, Mich.*	*Winkler, Tex.*	*Midway, Calif.*	*Conroe, Tex.*
Alkyl cyclopentanes	53	53	34	34	71	60	28
Alkyl cyclohexanes	47	47	66	66	29	40	72
Total	100	100	100	100	100	100	100

Table XI gives the relative amounts of the alkyl cyclopentanes and alkyl cyclohexanes, 40° to 102° C. As can be seen, the relative amounts of these two groups of components show little correlation, but rather appear to be characteristic of the crude, just as are the relative amounts of the normal paraffins and isoparaffins.

On the basis of the foregoing data, the following conclusions were drawn with regard to the composition of the gasoline fraction of different petroleums, to 102° C. for paraffins and naphthenes and to 160° C. for aromatics.

(*a*) The gasoline fraction of different crudes may be characterized by specifying the relative amounts of the following five classes of hydrocarbons: normal paraffins, isoparaffins, alkyl cyclopentanes, alkyl cyclohexanes, and aromatics.

(*b*) The gasoline fractions of different crudes are composed of the same hydrocarbons, the differences from one crude to another being essentially in the relative amounts of the foregoing five classes of hydrocarbons.

(*c*) Within each of these five classes, the individual hydrocarbons occur in proportions which are usually of the same order of magnitude for different naphthas.

(*d*) It appears possible to predict the order of magnitude of the amounts of the individual hydrocarbons, paraffins, and naphthenes, 40° to 102° C., and aromatics to 160° C., in an appropriate fraction of a given naphtha when there are known the relative amounts of the foregoing five classes of hydrocarbons, or alternatively for each class, the amount of one of the main components of that class.

While the eight possible aromatic hydrocarbons to 160° C. were relatively easily determined (from measurements of boiling-points, refractive indices, and freezing-points), the twelve possible aromatic hydrocarbons in the range 160° to 180° C. are present in such relatively smaller

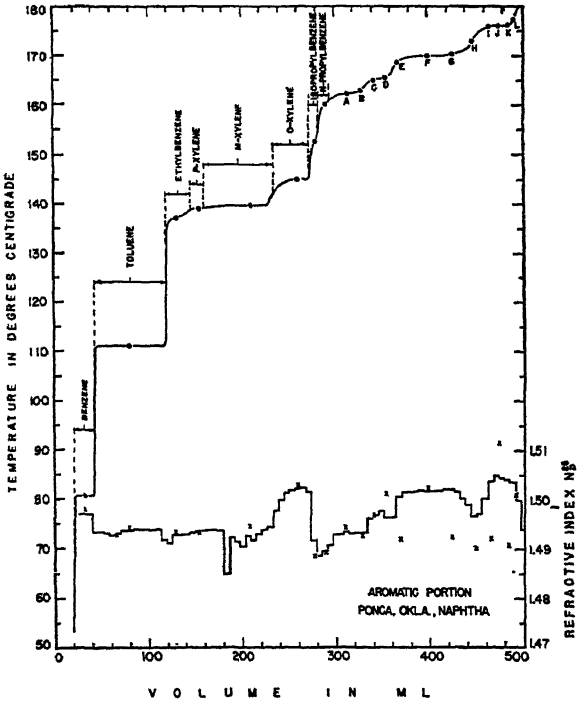


Fig. 30. Plot of the boiling-point and refractive index of the distillate from the analytical distillation of the aromatic portion of the Ponca, Okla., naphtha.

The scale of ordinates on the left gives the boiling-point at 770 mm. Hg. in °C. and that on the right the refractive index, N_D at 25° C. The scale of abscissae gives the volume of distillate in ml. The solid circles and crosses give the boiling-points and refractive indices, respectively, of the indicated pure components.

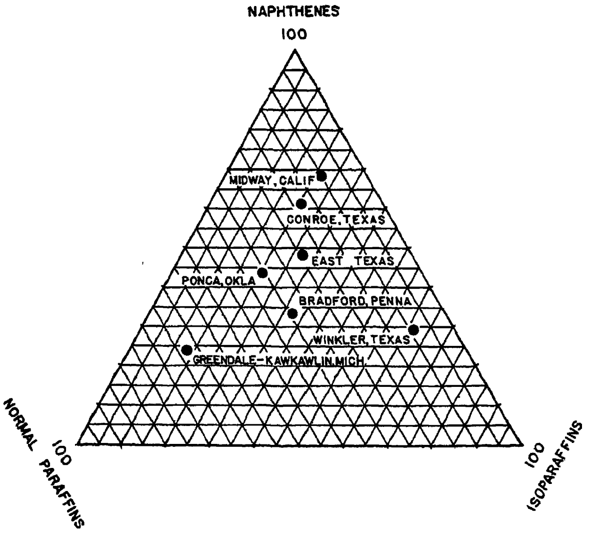


Fig. 31. Triangular plot showing the relation between the content of normal paraffins, isoparaffins, and naphthenes (cycloparaffins), for the distillate, 40° to 102° C., for seven representative naphthas.

amounts, and with such small differences in boiling-point, that it is possible to obtain from the boiling-point–volume curves on the quantity of material actually processed only values for pairs of components. Further, the lack of adequate amounts of nearly pure stocks of each of the component hydrocarbons made it impossible to utilize the method of determining individual hydrocarbons in mixtures of hydrocarbons by measurement of freezing-points [108]. It was evident, however, that the analysis of the individual aromatic hydrocarbons in the material above 160° C. could be performed successfully by spectrographic methods. Accordingly, the co-operation of three laboratories which had experience in the spectrographic analysis of the C_9 alkylbenzenes was enlisted. These laboratories were those of the Socony-Vacuum Oil Company, Paulsboro, N.J., the Standard Oil Development Company, Elizabeth, N.J., and the Sun Oil Company, Norwood, Pa. The Socony-Vacuum and Standard Oil Development laboratories agreed to make infra-red and the Sun Oil laboratory Raman spectral measurements.

Fig. 32 gives, for the C_9 aromatic portion of the Ponca, Oklahoma, naphtha, a plot of the boiling-point of the distillate as a function of its volume. These data are the same as those shown in the upper right portion of Fig. 30.

Tables XII and XIII give the amounts of the alkylbenzenes in the C_9 portion of the seven representative naphthas, expressed, respectively, as a percentage of the naphtha normally boiling in the range 40° to 180° C. and as a percentage of the crude petroleum. In Tables XII, XIII, and XIV the letters refer to the following naphthas: *A*, Ponca, Okla.; *B*, East Texas; *C*, Greendale-Kawkawlin, Mich.; *D*, Winkler, Texas; *E*, Midway, Calif.; *F*, Conroe, Texas.

Table XIV gives the relative amounts of the alkylbenzenes in the C_9 portion of the seven representative crudes.

The results indicate that the alkylbenzenes in the C_9 fraction of petroleum are present in relative amounts which are of the same magnitude for different crude petroleums,

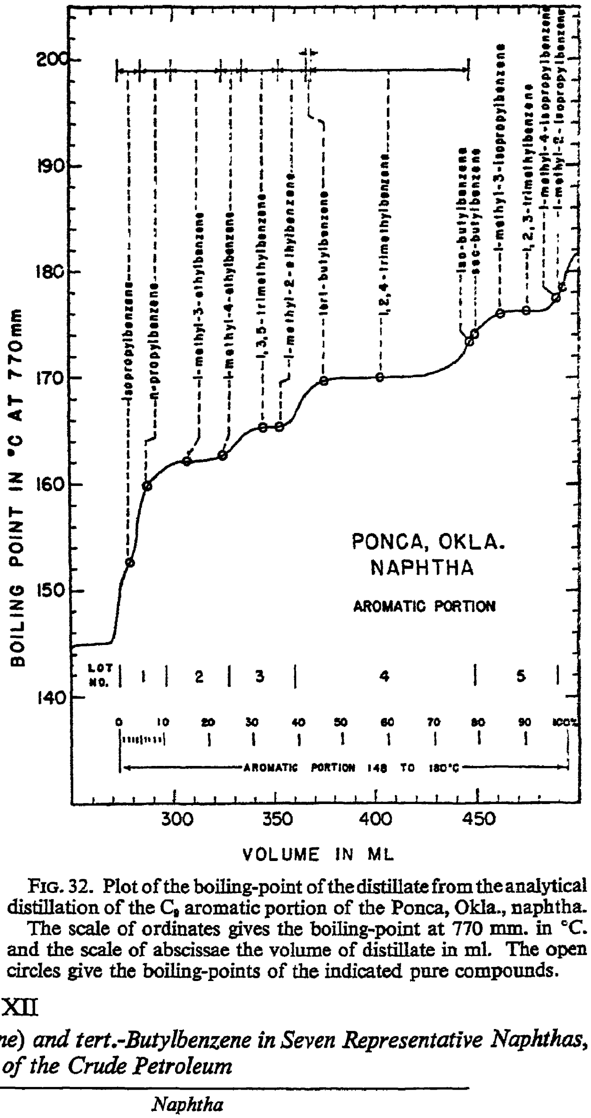


FIG. 32. Plot of the boiling-point of the distillate from the analytical distillation of the C_9 aromatic portion of the Ponca, Okla., naphtha. The scale of ordinates gives the boiling-point at 770 mm. in °C. and the scale of abscissae the volume of distillate in ml. The open circles give the boiling-points of the indicated pure compounds.

TABLE XII

Amounts of the C_9 Alkylbenzenes (except 1,2,3-Trimethylbenzene) and tert.-Butylbenzene in Seven Representative Naphthas, Expressed as a Percentage of the Crude Petroleum

Compound	*Naphtha*						
	A	*B*	*C*	*D*	*E*	*F*	*G*
	Percentage by volume of the crude petroleum						
Isopropylbenzene	0·07	0·04	0·03	0·03	0·03	0·03	0·09
n-Propylbenzene	0·09	0·08	0·05	0·03	0·02	0·04	0·12
1-Methyl-3-ethylbenzene	0·17	0·16	0·13	0·08	0·01	0·04	0·40
1-Methyl-4-ethylbenzene	0·06	0·07	0·05	0·03	0·05	0·03	0·13
1,3,5-Trimethylbenzene	0·12	0·09	0·17	0·05	0·05	0·05	0·36
1-Methyl-2-ethylbenzene	0·09	0·07	0·03	0·04	0·01	0·03	0·08
tert.-Butylbenzene	0·01	0·01	0·002	0·003	0·002	0·003	0·01
1,2,4-Trimethylbenzene	0·51	0·34	0·33	0·15	0·13	0·13	0·69

TABLE XIII

Amounts of the C_9 Alkylbenzenes (except 1,2,3-Trimethylbenzene) and tert.-Butylbenzene in Seven Representative Naphthas, Expressed as a Percentage of the Naphtha 40° to 180° C.

Compound	*Naphtha*						
	A	*B*	*C*	*D*	*E*	*F*	*G*
	Percentage by volume of the naphtha 40° to 180° C.						
Isopropylbenzene	0·22	0·12	0·11	0·13	0·22	0·19	0·33
n-Propylbenzene	0·29	0·28	0·18	0·15	0·13	0·21	0·46
1-Methyl-3-ethylbenzene	0·51	0·57	0·52	0·37	0·08	0·25	1·47
1-Methyl-4-ethylbenzene	0·19	0·26	0·19	0·13	0·34	0·17	0·49
1,3,5-Trimethylbenzene	0·35	0·32	0·68	0·22	0·40	0·31	1·34
1-Methyl-2-ethylbenzene	0·29	0·24	0·10	0·18	0·04	0·17	0·32
tert.-Butylbenzene	0·03	0·02	0·01	0·01	0·02	0·02	0·05
1,2,4-Trimethylbenzene	1·53	1·18	1·31	0·64	0·97	0·72	2·56

TABLE XIV

Relative Amounts of the C_9 Alkylbenzenes (except 1,2,3-Trimethylbenzene) and tert.-Butylbenzene in Seven Representative Naphthas

Compound	*A*	*B*	*C*	*D*	*E*	*F*	*G*	*Range of values*	*Average value*
	Relative amounts							*(rounded)*	
Isopropylbenzene	6·4	4·2	3·4	7·3	10·0	9·5	4·8	3 to 10	7
n-Propylbenzene	8·4	9·5	5·9	8·1	5·8	10·3	6·5	6 to 10	8
1-Methyl-3-ethylbenzene	15·0	19·0	16·8	20·2	3·8	12·4	21·0	4 to 21	15
1-Methyl-4-ethylbenzene	5·5	8·6	6·1	7·3	15·3	8·1	6·9	6 to 15	8
1,3,5-Trimethylbenzene	10·2	10·7	22·0	12·1	18·4	15·3	19·1	10 to 22	15
1-Methyl-2-ethylbenzene	8·5	8·0	3·3	9·6	1·8	8·1	4·5	2 to 10	6
tert.-Butylbenzene	1·0	0·8	0·2	0·7	0·7	0·7	0·7	0 to 1	1
1,2,4-Trimethylbenzene	45·0	39·2	42·3	34·7	44·2	35·6	36·5	35 to 45	40
Total									100

with the average values being as given in the last column of Table XIV. This follows similar relations for the lower alkylbenzenes and for certain other groups of hydrocarbons.

Complete details of the above work have been reported [81, 83, 108].

XVII. Current Work

With regard to its current work in this field, the A.P.I. Research Project 6 is completing the examination of the gasoline fraction (material below 177° C.), is exhaustively separating the material intermediate between the gasoline and kerosine fractions (177° to 200° C.), is exhaustively separating the aromatic-free part of the kerosine fraction (200° to 230° C.), and is beginning the separation of material of the gas-oil range (230° to 300° C.).

XVIII. Publications of the American Petroleum Institute Research Project 6 at the National Bureau of Standards

1. Apparatus and Methods for the Separation, Identification, and Determination of the Chemical Constituents of Petroleum. E. W. Washburn, J. H. Bruun, and M. M. Hicks. *J. Res. Nat. Bur. Standards*, **2**, 467 (1929).
2. Laboratory Rectifying Columns with Non-siphoning Bubbling-cap Plates. J. H. Bruun. *Ind. Eng. Chem., Anal. Ed.*, **1**, 212 (1929).
3. Convenient Reflux Regulator for Laboratory Stills. J. H. Bruun. *Ind. Eng. Chem., Anal. Ed.* **2**, 187 (1930).
4. The Principles of Measurement and Calculation in Their Application to the Determination of Diophantine Quantities. E. W. Washburn. *J. Res. Nat. Bur. Standards*, **4**, 221 (1930).
5. The Problem of Establishing the Identity and Purity of a Hydrocarbon obtained from Petroleum. E. W. Washburn. *Ind. Eng. Chem.* **22**, 985 (1930).
6. An Improved Victor-Meyer Molecular Weight Apparatus. M. M. Hicks-Bruun. *J. Res. Nat. Bur. Standards*, **5**, 575 (1930).
7. On the Determination of the Empirical Formula of a Hydrocarbon. E. W. Washburn. *J. Res. Nat. Bur. Standards*, **5**, 867 (1930).
8. Isolation of the Isomers of Hexane from Petroleum. J. H. Bruun and M. M. Hicks-Bruun. *J. Res. Nat. Bur. Standards*, **5**, 933 (1930).
9. Determination of the Toluene Content of a Mid-Continent Petroleum. J. H. Bruun, R. T. Leslie, and S. T. Schicktanz. *J. Res. Nat. Bur. Standards*, **6**, 363 (1931).
10. Separation of *n*-Octane from Petroleum by Distillation and Crystallization. R. T. Leslie and S. T. Schicktanz. *J. Res. Nat. Bur. Standards*, **6**, 377 (1931).
11. Determination of the Benzene and the Normal Hexane Content of a Mid-Continent Petroleum. J. H. Bruun and M. M. Hicks-Bruun. *J. Res. Nat. Bur. Standards*, **6**, 869 (1931).
12. Isolation and Determination of Cyclohexane in a Mid-Continent Petroleum. J. H. Bruun and M. M. Hicks-Bruun. *J. Res. Nat. Bur. Standards*, **7**, 607 (1931).
13. Isolation and Determination of Methylcyclopentane in a Mid-Continent Petroleum. M. M. Hicks-Bruun and J. H. Bruun. *J. Res. Nat. Bur. Standards*, **7**, 799 (1931).
14. Laboratory Rectifying Stills of Glass. J. H. Bruun and S. T. Schicktanz. *J. Res. Nat. Bur. Standards*, **7**, 851 (1931).
15. Isolation of *n*-Nonane from a Mid-Continent Petroleum. J. D. White and F. W. Rose, Jr. *J. Res. Nat. Bur. Standards*, **7**, 907 (1931).
16. What is Petroleum? Methods for the Isolation and Determination of the Chemical Constituents of Petroleum. J. H. Bruun. *J. Chem. Educ.* **8**, 1930 (1931).
17. Isolation and Determination of Normal Heptane and of Methylcyclohexane in a Mid-Continent Petroleum. Including a Determination of the Phase-equilibrium Diagram for the Condensed System Normal Heptane-methylcyclohexane. M. M. Hicks-Bruun and J. H. Bruun. *J. Res. Nat. Bur. Standards*, **8**, 525 (1932).
18. Isolation of *n*-Decane from Petroleum by Distillation and Equilibrium Melting. J. H. Bruun and M. M. Hicks-Bruun. *J. Res. Nat. Bur. Standards*, **8**, 583 (1932).
19. A Laboratory Apparatus for the Continuous Extraction of Liquids by Low-boiling Solvents. R. T. Leslie. *J. Res. Nat. Bur. Standards*, **8**, 591 (1932).
20. Note on the Probable Presence of 2,2-Dimethylpentane in a Mid-Continent Petroleum. J. H. Bruun and M. M. Hicks-Bruun. *J. Res. Nat. Bur. Standards*, **9**, 53 (1932).
21. Note on the Freezing Point of Iso-octane (2,2,4-Trimethylpentane). J. H. Bruun and M. M. Hicks-Bruun. *J. Res. Nat. Bur. Standards*, **9**, 269 (1932).
22. The Synthesis, Purification, and Certain Physical Constants of the Normal Hydrocarbons from Pentane to Dodecane, of *n*-Amyl-Bromide and *n*-Nonyl Bromide. B. J. Mair. *J. Res. Nat. Bur. Standards*, **9**, 457 (1932).
23. Isolation of the Three Xylenes from an Oklahoma Petroleum. J. D. White and F. W. Rose, Jr. *J. Res. Nat. Bur. Standards*, **9**, 711 (1932).
24. A Multi-range Potentiometer and its Application to the Measurement of Small Temperature Differences. H. B. Brooks and A. W. Spinks. *J. Res. Nat. Bur. Standards*, **9**, 781 (1932).
25. 1,1-Dimethylcyclopentane and 2-Methylhexane in a Mid-Continent Petroleum. J. H. Bruun and M. M. Hicks-Bruun. *J. Res. Nat. Bur. Standards*, **10**, 465 (1933).
26. Purification of Hydrocarbons by Crystallization from Liquid Methane. Isolation of 2-Methylheptane from Petroleum. R. T. Leslie. *J. Res. Nat. Bur. Standards*, **10**, 609 (1933).
27. Isolation of Ethylbenzene from an Oklahoma Petroleum. J. D. White and F. W. Rose, Jr. *J. Res. Nat. Bur. Standards*, **10**, 639 (1933).
28. Spectral Differentiation of Petroleum Hydrocarbons. U. Liddel and C. Kasper. *J. Res. Nat. Bur. Standards*, **11**, 599 (1933).
29. Fractionation of Petroleum into its Constituent Hydrocarbons. E. W. Washburn. *Ind. Eng. Chem.* **25**, 891 (1933).
30. Note on an Improved Chain-packed Distilling Column. S. T. Schicktanz. *J. Res. Nat. Bur. Standards*, **11**, 89 (1933).
31. A Simple Calorimeter for Heats of Fusion. Data on the Fusion of Pseudocumene, Mesitylene (α and β), Hemimellitene, *o*- and *m*-Xylene, and on Two Transitions of Hemimellitene. F. D. Rossini. *J. Res. Nat. Bur. Standards*, **11**, 553 (1933).
32. The Isolation of Mesitylene, Pseudocumene, and Hemimel-

litene from an Oklahoma Petroleum. B. J. Mair and S. T. Schicktanz. *J. Res. Nat. Bur. Standards,* **11,** 665 (1933).

33. Chemical Constituents of Petroleum. A.P.I. Research Project 6. E. W. Washburn. *Proc. A.P.I.* **14,** (III), 111 (1933).
34. A Fractionating Column with Fritted Glass Plates. S. T. Schicktanz. *J. Res. Nat. Bur. Standards,* **12,** 259 (1934).
35. The Critical Solution Temperatures of some Hydrocarbons in Sulphur Dioxide. R. T. Leslie. *J. Res. Nat. Bur. Standards,* **13,** 589 (1934).
36. The Isolation of a Nonanaphthene from an Oklahoma Petroleum. J. D. White and F. W. Rose, Jr. *J. Res. Nat. Bur. Standards,* **13,** 799 (1934).
37. An Accurate Ebullioscopic Method for the Determination of the Molecular Weights of Non-volatile Petroleum Fractions. B. J. Mair. *J. Res. Nat. Bur. Standards,* **14,** 345 (1935).
38. An Apparatus for Measuring the Boiling-Points of Lubricating Oils and Other Compounds of High Molecular Weight at Reduced Pressures. S. T. Schicktanz. *J. Res. Nat. Bur. Standards,* **14,** 685 (1935).
39. Separation of a Dimethylcyclohexane Fraction from a Mid-Continent Petroleum. R. T. Leslie. *J. Res. Nat. Bur. Standards,* **15,** 41 (1935).
40. Separation of Petroleum Hydrocarbons with Silica Gel. B. J. Mair and J. D. White. *J. Res. Nat. Bur. Standards,* **15,** 51 (1935).
41. Isolation of Ethylcyclohexane from a Mid-Continent Petroleum. F. W. Rose, Jr., and J. D. White. *J. Res. Nat. Bur. Standards,* **15,** 151 (1935).
42. Present Status of the Isolation and Identification of the Volatile Hydrocarbons in a Mid-Continent Petroleum. R. T. Leslie and J. D. White. *J. Res. Nat. Bur. Standards,* **15,** 211 (1935).
43. Apparatus and Methods for Investigating the Chemical Constitution of Lubricating Oil and the Preliminary Fractionation of the Lubricating-oil Fraction of a Mid-Continent Petroleum. B. J. Mair, S. T. Schicktanz, and F. W. Rose, Jr. *J. Res. Nat. Bur. Standards,* **15,** 557 (1935).
44. The Chemical Constitution of the Gasoline Fraction of Petroleum. A.P.I. Research Project 6. F. D. Rossini. *Proc. A.P.I.,* **16** M (III), 47 (1935); *Oil and Gas J.* **33,** no. 52, 61 (1935); *Refiner and Natural Gasoline Mfr.* **14,** 255 (1935).
45. Fundamental Research on the Chemical Constitution of Lubricating Oil. A.P.I. Research Project 6. F. D. Rossini. *Proc. A.P.I.,* **16** M (III), 63 (1935); *Oil and Gas J.* **34,** no. 6, 41 (1935); *Refiner and Natural Gasoline Mfr.* **14,** 266 (1935).
46. Composition of Petroleum Wax. B. J. Mair and S. T. Schicktanz. *Ind. Eng. Chem.* **28,** 1056 (1936).
47. Hydrocarbons in the Fraction of a Mid-Continent Petroleum Distilling between 115° and 124° C. R. T. Leslie. *J. Res. Nat. Bur. Standards,* **17,** 761 (1936).
48. Extraction, with Acetone, of Substantially Constant-boiling Fractions of a 'Water-white' Lubricating Oil. B. J. Mair and S. T. Schicktanz. *Ind. Eng. Chem.* **28,** 1446 (1936); *J. Res. Nat. Bur. Standards,* **17,** 909 (1936).
49. Relationships between the Physical Properties and Chemical Constitution of Lubricating-oil Fractions. B. J. Mair and C. B. Willingham. *Ind. Eng. Chem.* **28,** 1452 (1936); *J. Res. Nat. Bur. Standards,* **17,** 923 (1936).
50. Isolation of an Isononane from Petroleum.—Its Fractionation from Naphthenes by Distillation with Acetic Acid. J. D. White and F. W. Rose, Jr. *J. Res. Nat. Bur. Standards,* **17,** 943 (1936).
51. The Chemical Constituents of Lubricating Oil.—A.P.I. Research Project 6. F. D. Rossini. *Proc. A.P.I.,* **17** (III), 59 (1936); *Oil and Gas J.* **35,** no. 26, 146 (1936); *Refiner and Natural Gasoline Mfr.* **15,** 499 (1936).
52. Separation of Constant-boiling Mixtures of Naphthene and Paraffin Hydrocarbons by Distillation with Acetic Acid. S. T. Schicktanz. *J. Res. Nat. Bur. Standards,* **18,** 129 (1937).
53. Study of the Crystal Behaviour of Hydrocarbons. R. T. Leslie and W. W. Heuer. *J. Res. Nat. Bur. Standards,* **18,** 639 (1937).
54. Infra-red Absorption of 19 Hydrocarbons, including 10 of High Molecular Weight. F. W. Rose, Jr. *J. Res. Nat. Bur. Standards,* **19,** 143 (1937).
55. Separation of the Three Methyloctanes from Mid-Continent Petroleum. J. D. White and A. R. Glasgow, Jr. *J. Res. Nat. Bur. Standards,* **19,** 423 (1937).
56. Study of Ball Packings for Laboratory Rectifying Columns. A. R. Glasgow, Jr., and S. T. Schicktanz. *J. Res. Nat. Bur. Standards,* **18,** 593 (1937).
57. A Decade of Research on the Chemical Constitution of Petroleum. F. D. Rossini. *Proc. A.P.I.* **18** (III), 36 (1937); *Oil and Gas. J.* **36,** no. 26, 193 (1937); *Refiner and Natural Gasoline Mfr.* **16,** no. 11, 545 (1937).
58. A Laboratory Extraction Apparatus and its Use in Separating a Lubricating-oil Fraction with Acetic Acid. S. T. Schicktanz. *J. Res. Nat. Bur. Standards,* **20,** 83 (1938).
59. Quantitative Analysis, with respect to the Component Structural Groups, of the Infra-red (1 to 2 mu) Molal Absorptive Indices of 55 Hydrocarbons. F. W. Rose, Jr. *J. Res. Nat. Bur. Standards,* **20,** 129 (1938).
60. Separation of Isopropylbenzene from a Mid-Continent Petroleum by Adsorption with Silica Gel and Distillation with Acetic Acid. J. D. White and F. W. Rose, Jr. *J. Res. Nat. Bur. Standards,* **21,** 151 (1938).
61. Separation, by Distillation with Acetic Acid of the Aromatic Hydrocarbons from the Fraction of a Mid-Continent Petroleum Boiling between 154° and 162° C. F. W. Rose, Jr., and J. D. White. *J. Res. Nat. Bur. Standards,* **21,** 167 (1938).
62. A Continuous High-vacuum Still and Boiling-point Apparatus, and the Systematic Distillation of a Dewaxed Lubricant Fraction of Petroleum. R. T. Leslie and W. W. Heuer. *J. Res. Nat. Bur. Standards,* **21,** 515 (1938).
63. Exhaustive Fractionation, by Distillation and Extraction, of the Extract Portion of the Lubricant Fraction from a Mid-Continent Petroleum. B. J. Mair and C. B. Willingham. *J. Res. Nat. Bur. Standards,* **21,** 535 (1938).
64. Hydrogenation of the Extract Portion of the Lubricant Fraction from a Mid-Continent Petroleum. B. J. Mair, C. B. Willingham, and A. J. Streiff. *J. Res. Nat. Bur. Standards,* **21,** 565 (1938).
65. Chemical Constitution of the Extract Portion of the Lubricant Fraction from a Mid-Continent Petroleum. B. J. Mair, C. B. Willingham, and A. J. Streiff. *J. Res. Nat. Bur. Standards,* **21,** 581 (1938).
66. Hydrocarbons in the Lubricant Fraction of Petroleum. F. D. Rossini. *Proc. A.P.I.* 19 (III), 99 (1938); *Oil and Gas J.* **37,** no. 27, 141 (1938); *Refiner and Natural Gasoline Mfr.* **17,** no. 11, 557 (1938).
67. Separation of 1,2,4-Trimethylcyclohexane and an Isononane from a Mid-Continent Petroleum. J. D. White and A. R. Glasgow, Jr. *J. Res. Nat. Bur. Standards,* **22,** 137 (1939).
68. Summary of an Investigation of the Composition of a Mid-Continent Petroleum Distillate, Boiling between 100° and 130° C. R. T. Leslie. *J. Res. Nat. Bur. Standards,* **22,** 153 (1939).
69. 2,6-Dimethylheptane: Its Synthesis, Properties, and Comparison with an Isononane from Petroleum. J. D. White, F. W. Rose, Jr., G. Calingaert, and H. Soroos. *J. Res. Nat. Bur. Standards,* **22,** 315 (1939).
70. Separation of Hydrocarbons of High Molecular Weight by Adsorption on Silica Gel. C. B. Willingham. *J. Res. Nat. Bur. Standards,* **22,** 321 (1939).
71. Efficiency of a Rotary Distillation Column. B. J. Mair and C. B. Willingham. *J. Res. Nat. Bur. Standards,* **22,** 519 (1939).
72. Reflux Regulator and Head for Laboratory Rectifying Columns. F. D. Rossini and A. R. Glasgow, Jr. *J. Res. Nat. Bur. Standards,* **23,** 509 (1939).
73. Separation of the Aromatic Hydrocarbons, and the Isolation of *n*-Dodecane, Naphthalene, 1-Methylnaphthalene, and 2-Methylnaphthalene, from the Kerosine Fraction of Petroleum. B. J. Mair and A. J. Streiff. *J. Res. Nat. Bur. Standards,* **24,** 395 (1940).
74. Isolation of 3-Methylhexane, *trans*-1,2-Dimethylcyclopentane, and *trans*-1,3-Dimethylcyclopentane from Petroleum. A. R. Glasgow, Jr. *J. Res. Nat. Bur. Standards,* **24,** 509 (1940).
75. Use of Azeotropic Distillation in Separating Hydrocarbons from Petroleum. F. D. Rossini, B. J. Mair, and A. R. Glasgow, Jr. *Proc. A.P.I.* **21** (III) 43 (1940).
76. Determination of Freezing Points and Amounts of Impurity in Hydrocarbons from Freezing and Melting Curves. B. J. Mair, A. R. Glasgow, Jr., and F. D. Rossini. *J. Res. Nat. Bur. Standards,* **26,** 591 (1941).
77. Separation of Hydrocarbons by Azeotropic Distillation. B. J. Mair, A. R. Glasgow, Jr., and F. D. Rossini. *J. Res. Nat. Bur. Standards,* **27,** 39 (1941).
78. Isolation of 1,2,3,4-Tetramethylbenzene, 5,6,7,8-Tetrahydronaphthalene, 1-Methyl-5,6,7,8-tetrahydronaphthalene, and 2-Methyl-5,6,7,8-tetrahydronaphthalene from Petroleum. B. J. Mair and A. J. Streiff. *J. Res. Nat. Bur. Standards,* **27,** 343 (1941).
79. Progress Report on the Hydrocarbons in the Kerosine Fraction of Petroleum. A.P.I. Research Project 6. F. D. Rossini and B. J. Mair. *Proc. A.P.I.* **22** (III), 6 (1941); *Oil and Gas J.* **40,** no. 26, 129 (1941); *Refiner and Natural Gasoline Mfr.* **20,** no. 11, 494 (1941).
80. Hydrocarbons in Petroleum. F. D. Rossini. *Record Chem. Progress,* 3, 53 (1942).
81. Method for Analyzing the Gasoline Fraction of Petroleum,

with Preliminary Results on East Texas and Oklahoma Crudes. F. D. Rossini, B. J. Mair, A. F. Forziati, A. R. Glasgow, Jr., and C. B. Willingham. *Proc. A.P.I.* **23** (III), 8 (1942).

82. Hydrocarbons in Petroleum. F. D. Rossini. *Petroleum Engr.* **14,** 223 (1943).
83. Hydrocarbons in the Gasoline Fraction of Seven Representative Crudes including all the Distillate to 102° C. and the Aromatics to 160° C. A. F. Forziati, C. B. Willingham, B. J. Mair, and F. D. Rossini. *Proc. A.P.I.* **24** (III), 34 (1943); *J. Res. Nat. Bur. Standards,* **32,** 11 (1944).
84. Note on the Macroanalysis of Carbon and Hydrogen by Combustion. D. D. Wagman and F. D. Rossini. *J. Res. Nat. Bur. Standards,* **32,** 95 (1944).
85. Analytical Determination of Aromatic Hydrocarbons by Adsorption. B. J. Mair and A. F. Forziati. *J. Res. Nat. Bur. Standards,* **32,** 151 (1944).
86. Separation and Recovery of Aromatic Hydrocarbons from Paraffins and Naphthenes by Adsorption. B. J. Mair and A. F. Forziati. *J. Res. Nat. Bur. Standards,* **32,** 165 (1944).
87. Method for Determining Individual Hydrocarbons in Mixtures of Hydrocarbons by Measurement of Freezing-points. A. J. Streiff and F. D. Rossini. *J. Res. Nat. Bur. Standards,* **32,** 185 (1944).
88. Theoretical Analysis of Certain Time-temperature Freezing and Melting Curves as applied to Hydrocarbons. W. J. Taylor and F. D. Rossini. *J. Res. Nat. Bur. Standards,* **32,** 197 (1944).
89. Improved Reflux Regulator and Head for Laboratory Distilling Columns. C. B. Willingham and F. D. Rossini. *J. Res. Nat. Bur. Standards,* **33,** 383 (1944).
90. Separation and Determination of Aromatic and Mono-olefine Hydrocarbons in Mixtures with Paraffins and Naphthenes by Adsorption. B. J. Mair. *J. Res. Nat. Bur. Standards,* **34,** 435 (1945).
91. Vapour Pressures and Boiling-points of some Paraffin, Alkyl cyclopentane, Alkylcyclohexane, and Alkylbenzene Hydrocarbons. C. B. Willingham, W. J. Taylor, J. M. Pignocco, and F. D. Rossini. *J. Res. Nat. Bur. Standards,* **35,** 219 (1945).
92. Determination of the Purity of Hydrocarbons by Measurement of Freezing Points. A. R. Glasgow, Jr., A. J. Streiff, and F. D. Rossini. *J. Res. Nat. Bur. Standards,* **35,** 355 (1945).
93. Assembly and Calibration of a Density Balance for Liquid Hydrocarbons. A. F. Forziati, B. J. Mair, and F. D. Rossini. *J. Res. Nat. Bur. Standards,* **35,** 513 (1945).
94. Purification and Properties of 29 Paraffin, 4 Alkylcyclopentane, 10 Alkylcyclohexane, and 8 Alkylbenzene Hydrocarbons. A. F. Forziati, A. R. Glasgow, Jr., C. B. Willingham, and F. D. Rossini. *J. Res. Nat. Bur. Standards,* **36,** 129 (1946).
95. Assembly, Testing, and Operation of Laboratory Distilling Columns of High Efficiency. C. B. Willingham and F. D. Rossini. *J. Res. Nat. Bur. Standards,* **37,** 15 (1946).
96. Purification, Purity, and Freezing Points of 31 Hydrocarbons of the API-NBS Series. A. R. Glasgow, Jr., E. T. Murphy, C. B. Willingham, and F. D. Rossini. *J. Res. Nat. Bur. Standards,* **37,** 141 (1946).
97. Laboratory Distilling Columns of High Efficiency used in the Work of the A.P.I. Research Project 6. C. B. Willingham and F. D. Rossini. *Proc. A.P.I.* **26** (III), 1 (1946).
98. Analysis of Alkylates and Hydrocodimers. A. R. Glasgow, Jr., A. J. Streiff, C. B. Willingham, and F. D. Rossini. *Proc. A.P.I.* **26** (III), 127 (1946).
99. Proposed Method of Test for Aromatic Hydrocarbons in Mixtures with Naphthenes and Paraffins by Silica Gel Adsorption. B. J. Mair and F. D. Rossini. Report issued 31 Dec. 1945. In revised form, appears in A.S.T.M. Committee D-2 Standards, *Year Book on Petroleum Products and Lubricants,* p. 20 (Dec. 1946).
100. Purification, Purity, and Freezing Points of 7 Heptanes, 16 Octanes, 6 Pentenes, Cyclopentene, and 7 C_9H_{12} Alkylbenzenes of the API-Standard and API-NBS Series. A. J. Streiff, E. T. Murphy, V. A. Sedlak, C. B. Willingham, and F. D. Rossini. *J. Res. Nat. Bur. Standards,* **37,** 331 (1946).
101. Hydrocarbons in Petroleum. F. D. Rossini. *Chem. Eng. News,* **25,** 230 (1947).
102. Purification, Purity, and Freezing Points of 8 Nonanes, 11 Alkylcyclopentanes, 6 Alkylcyclohexanes, and 4 Butylbenzenes of the API-Standard and API-NBS Series. A. J. Streiff, E. T. Murphy, J. C. Cahill, H. F. Flanagan, V. A. Sedlak, C. B. Willingham, and F. D. Rossini. *J. Res. Nat. Bur. Standards,* **38,** 53 (1947).
103. Fractionation and Analysis of Hydrocarbons by Adsorption. B. J. Mair. *Ann. N.Y. Acad. Sci.* **49,** 218 (1948).
104. Rotary Concentric-tube Distilling Column. C. B. Willingham, V. A. Sedlak, J. W. Westhaver, and F. D. Rossini. *Ind. Eng. Chem.* **39,** 706 (1947).
105. Hydrocarbons in the 102° to 108° C. Fraction of Petroleum. A. R. Glasgow, Jr., C. B. Willingham, and F. D. Rossini. *J. Res. Nat. Bur. Standards,* **39,** 621 (1947).
106. Alkylbenzenes in the C_8 Fraction from Five Different Catalytic Petroleum Refining Processes. A. J. Streiff and F. D. Rossini. *J. Res. Nat. Bur. Standards,* **39,** 303 (1947).
107. Assembly and Testing of a 52-foot Laboratory Adsorption Column. Separation of Hydrocarbons by Adsorption. B. J. Mair, A. L. Gaboriault, and F. D. Rossini. *Ind. Eng. Chem.* **39,** 1072 (1947).
108. Alkylbenzenes in the C_9 Fraction of Seven Representative Crudes. A. F. Forziati and F. D. Rossini. *J. Res. Nat. Bur. Standards,* **39,** 425 (1947).
109. *Scientific and Technical Services of the National Bureau of Standards for the Petroleum Industry.* F. D. Rossini. (1947.)
110. Purification, Purity, and Freezing Points of *n*-Decane, 4 Alkylcyclopentanes, 9 Alkylcyclohexanes, 2 Mono-olefines, 1,2-Butadiene, and 2-Butyne of the API-Standard and API-NBS series. A. J. Streiff, E. T. Murphy, J. C. Cahill, L. F. Soule, V. A. Sedlak, C. B. Willingham, and F. D. Rossini. *J. Res. Nat. Bur. Standards* **39,** 321 (1947).

CHEMICAL THERMODYNAMIC PROPERTIES OF HYDROCARBONS

By FREDERICK D. ROSSINI
National Bureau of Standards

I. Introduction

In September 1942 the American Petroleum Institute and the National Bureau of Standards began a co-operative programme on the collection, analysis, calculation, and compilation of data on the properties of hydrocarbons. This work, carried on as the A.P.I. Research Project 44, has resulted in the preparation of extensive tables of physical and thermodynamic properties, and catalogues of spectrographic properties, of hydrocarbons and related compounds.[1] As of 31 March 1947, there have been issued under this programme, in loose-leaf form, 344 pages of numerical data on the physical and thermodynamic properties, 3 pages of values of constants, 7 pages of values of conversion factors, 1 page of equations, 16 pages of molecular weights, 568 pages of material in the catalogue of infra-red spectrograms, and 172 pages of material in the catalogue of ultra-violet spectrograms. Catalogues of Raman and mass spectral data are in process of preparation.

The properties for which selected values are in process of compilation by the A.P.I. Research Project 44 include the following:

Boiling-point, and pressure coefficient of the boiling-point
Refractive index
Density and specific gravity
Freezing-point
Molecular volume
Molecular and specific refraction
Specific dispersion
Refractivity intercept
Viscosity
Critical constants
P-V-T relations
Vapour pressures
Heat and entropy of vaporization
Heat of combustion
Heat content
Free energy function
Entropy
Heat capacity
Heat of formation
Free energy of formation
Equilibrium constant of formation
Heat and entropy of fusion
Cryoscopic constants
Heat of transition.

The attached Table I lists the number of pages which have been issued, as of 31 March 1947, under the various properties and groups of compounds. Table II is a reproduction of the table giving the free energy of formation, to 1,500° K. of the alkylbenzenes C_8 to C_9.

The purpose of the present report is to summarize, in terms of selected representative reactions, the results of appropriate combinations of the values of heats of formation, free energies of formation, and the logarithm of the equilibrium constants of formation given, for the different hydrocarbons and related compounds, in the *w*, *x*, and *y* tables of the A.P.I. Research Project 44.

The fundamental thermodynamic properties may be taken as

E, the internal or intrinsic energy,
S, the entropy, *P*, the pressure,
V, the volume, and *T*, the temperature.

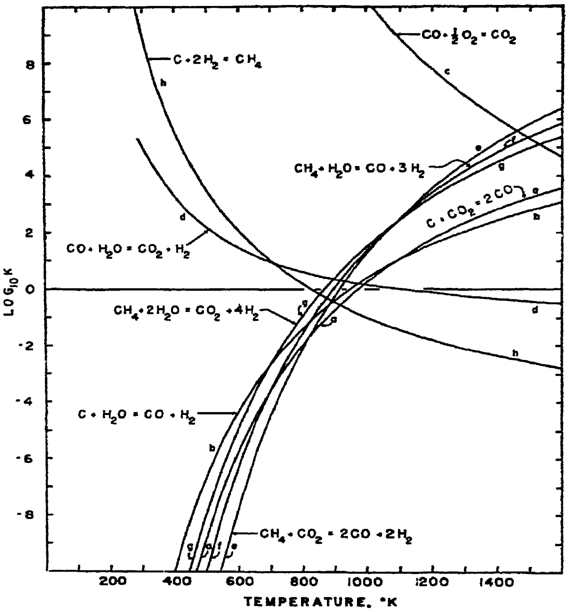


Fig. 1. Plot of the logarithm of the equilibrium constant for eight reactions involving O_2, H_2, H_2O, C(graphite), CO, CO_2, and CH_4.

The scale of ordinates gives the logarithm (to the base 10) of the equilibrium constant, $\log_{10}K$, for the given reaction. The scale of abscissae gives the temperature in °K. The curves apply to the following reactions:

(*a*) C(solid, graphite) + CO_2(gas) = 2CO(gas).
(*b*) C(solid, graphite) + H_2O(gas) = CO(gas) + H_2(gas).
(*c*) CO(gas) + $\frac{1}{2}O_2$(gas) = CO_2(gas).
(*d*) CO(gas) + H_2O(gas) = CO_2(gas) + H_2(gas).
(*e*) CH_4(gas) + CO_2(gas) = 2CO(gas) + $2H_2$(gas).
(*f*) CH_4(gas) + H_2O(gas) = CO(gas) + $3H_2$(gas).
(*g*) CH_4(gas) + $2H_2O$(gas) = CO_2(gas) + $4H_2$(gas).
(*h*) C(solid, graphite) + $2H_2$(gas) = CH_4(gas).

For convenience, the heat content or enthalpy is defined as

$$H = E + PV \qquad (1)$$

and the free energy as

$$F = E + PV - TS = H - TS. \qquad (2)$$

For the reaction occurring at constant temperature,[2]

$$\Delta F = \Delta H - T\Delta S. \qquad (3)$$

The equilibrium constant and the standard change in free energy are related as follows:[2]

$$\Delta F.^\circ = -RT\ln K,$$

where $\Delta F.$ is the increment in free energy for the reaction, with each reactant and product in its thermodynamic standard state, *R* is the gas constant (per mole), *T* is the absolute temperature, and *K* is the equilibrium constant.

---

[1] At this writing, the staff of the A.P.I. Research Project 44 is composed of seven persons at the National Bureau of Standards and two persons at the University of California (with Prof. K. S. Pitzer as Associate Director).

[2] See G. N. Lewis and M. Randall, *Thermodynamics and the Free Energy of Chemical Substances* (McGraw-Hill Book Co., New York, 1923).

TABLE I

AMERICAN PETROLEUM INSTITUTE RESEARCH PROJECT 44

Status of Tables of Physical and Thermodynamic Properties of Hydrocarbons
As of 31 March 1947

COMPOUNDS	No.	00	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	
	Name	O, H, N, C	O_2, H_2, OH, H_2O, N_2, NO, C, CO, CO_2	*Paraffins*, C_1 *to* C_5	*Paraffins*, C_6 *and* C_7	*Paraffins*, C_8	*Paraffins*, C_9	*Alkyl benzenes*, C_6 *to* C_9	*Alkyl cyclopentanes*, C_5 *to* C_7	*Alkyl cyclohexanes*, C_6 *to* C_8	*Mono-olefines*, C_2 *to* C_6	*Mono-olefines*, C_7	*Mono-olefines*, C_8	*Diolefines*, C_3 *to* C_6	*Acetylenes*, C_2 *to* C_5	*Styrenes*, C_8 and C_9	*Alkyl benzenes*, C_{10}	*Alkyl cyclopentanes*, C_8	*Alkyl cyclohexanes*, C_9	*Paraffins*, C_{10}	*Alkyl cyclopentenes*, C_5 *to* C_7	*Alkyl cyclohexenes*, C_6 *to* C_8	*Normal paraffins*	*Normal alkyl benzenes*	*Normal alkyl cyclopentanes*	*Normal alkyl cyclohexanes*	*Normal mono-olefines (1-alkenes)*	*Normal acetylenes (1-alkynes)*	*Total*
PROPERTIES		*Number in block indicates number of pages*																											
Name	*Letter*																												
B.p. in °C. at 760 mm. Hg; *dt/dp* in °C./mm. Hg; R.I., n_D, and density in g./ml., at 20° C. and 25° C.; f.p. in °C. at 1 atm.	a			1	2	1	2	1	1	1	2	2	5	2	1	1	1	1											24
B.p. in °F. at 29·921 in. Hg; *dt/dp* in °F./in. Hg; R.I., n_D, at 68°, 77° F.; density in lb./cu. ft., lb./gal. at 60°, 68°, 77° F.; sp. gr. (60° F./60° F.); f.p. in °F. at 1 atm.	a–E			1	2	1	2	1	1	1	2	2	5	2	1	1	1	1											24
Molecular volume and refraction in ml./mole; specific refraction and dispersion in ml./g.; refractivity intercept; all at 20° and 25° C.	b			1	2	1	2	1	1	1	2	2	5	2	1	1	1	1											24
Viscosity (absolute) in centipoise at given temperatures in °C.	c																						4						4
Kinematic viscosity in centistokes at given temperatures in °C.	c–K																						4						4
Kinematic viscosity in centistokes at given temperatures in °F.	c–E																												
Critical constants	i																												
P-V-T relations	j																												
Vapour pressures and boiling-points in °C.; at 10 to 1,500 mm. Hg.	k			1	2	2		2	1	2	1																		11
Vapour pressures and boiling-points (lb./sq. in.; °F.)	k–E																												

Heat of vaporization, ΔHv, at 25° C. and b.p. in k.cal./mole, cal./g., and B.Th.U./lb. Entropy of vaporization, ΔSv, at b.p. in cal./deg. mole	m			½	½	1	1	1	1	1	1																		7
Heat of combustion, $\Delta Hc°$, at 25° C., for liquid and gas, in k.cal./mole, cal./g., and B.Th.U./lb.	n		1	1	1	1		1			2	2			1								1	1	1	1	1	1	16
Heat of formation, $\Delta Hf°$, and free energy of formation, $\Delta Ff°$, in k.cal./mole; entropy, $S°$, in cal./deg. mole, all for liquid and gas, at 25° C.	p		1	1	1	1		1			2				1								1	1			1	1	12
Std. heat of vaporization, $\Delta Hv°$, and free energy of vaporization, $\Delta Fv°$, in k.cal./mole, at 25° C. Std. entropy of vaporization, $\Delta Sv°$, in cal./deg. mole, at 25° C.	q			½	½	1		1		1																			4
Heat content function, $(H°-H°_0)/T$, to 1,500° K., in cal./deg. mole	r	1	1	1	2	1		1			3				1								1	1	1	1	1	1	17
Free energy function, $(F°-H°_0)/T$, to 1,500° K., in cal./deg. mole	s	1	1	1	2	1		1			3				1								1	1	1	1	1	1	17
Entropy, $S°$, to 1,500° K., in cal./deg. mole	t	1	1	1	2	1		1			3				1								1	1	1	1	1	1	17
Heat content, $H°-H°$, to 1,500° K., in cal./mole	u	1	1	1	2	1		1			3				1								1	1	1	1	1	1	17
Heat content, $H°-H°_0$, to 2,200° F., in B.Th.U./lb.	u–E		1	1	2	2		2			4				1								2	2			2	2	21
Heat content, $H°-H°_0$, to 1,200° C., in cal./g.	u–G		1	1	2	1		1			3				1								1	1			1	1	14
Heat capacity, $C_P°$, to 1,500° K., in cal./deg. mole	v	1	1	1	2	1		1			3				1								1	1	1	1	1	1	17
Heat capacity, $C_P°$, to 2,200° F., in B.Th.U./lb. °F.	v–E		1	1	2	1		2			4				1								2	2			2	2	20
Heat capacity, C °, to 1,200° C., in cal./g. °C.	v–G		1	1	2	1		1			3				1								1	1			1	1	14
Heat of formation, $\Delta Hf°$, to 1,500° K., in k.cal./mole	w	1	1	1	2	1		1			3				1								1	1	1	1	1	1	17
Free energy of formation, $\Delta Ff°$, to 1,500° K., in k.cal./mole	x	1	1	1	2	1		1			3				1								1	1	1	1	1	1	17
Logarithm of equilibrium constant of formation, $\log_{10} Kf$, to 1,500° K.	y	1	1	1	2	1		1			3				1								1	1	1	1	1	1	17
Heat of fusion, $\Delta Hm°$, in k.cal./mole; entropy of fusion, $\Delta Sm°$, in cal./deg. mole; cryoscopic constants (A, B) Freezing-point in °C. and °K. at 1 atm.	z			1	2	1		1	1	1	2																		9
Total		8	14	20	37	23	7	24	6	8	52	8	15	6	17	3	3	3					24	16	9	9	16	16	344
Values of fundamental constants	α																												3
Conversion factors	β																												7
Useful equations with numerical constants	γ																												1
Molecular weights	δ																												15

TABLE II

Reproduction of the Table giving the Free Energy of Formation of the C_6 to C_9 Alkylbenzenes, to 1,500° K.

SELECTED VALUES OF PROPERTIES OF HYDROCARBONS

American Petroleum Institute Research Project 44

National Bureau of Standards *Washington, D.C.*

TABLE 5x. ALKYL BENZENES, C_6 TO C_9

FREE ENERGY OF FORMATION, Δ*Ff*°, AT 0° TO 1,500° K.

30 November 1945

Compound (gas)	*Formula*	*Temperature* in °K.*														
		0	*298·16*	*300*	*400*	*500*	*600*	*700*	*800*	*900*	*1,000*	*1,100*	*1,200*	*1,300*	*1,400*	*1,500*
		Free energy of formation,†, ΔFf°, in k.cal./mole‡														
Benzene	C_6H_6	24·000	30·989	31·058	35·008	39·242	43·663	48·211	52·838	57·537	62·270	67·02	71·79	76·57	81·34	86·11
Methylbenzene (Toluene)	C_7H_8	17·500	29·228	29·335	35·390	41·811	48·477	55·306	62·236	69·255	76·320	83·40	90·50	97·61	104·71	111·81
Ethylbenzene	C_8H_{10}	13·917	31·208	31·357	39·741	48·554	57·646	66·921	76·302	85·779	95·303	104·84	114·39	123·95	133·48	143·02
1,2-Dimethylbenzene (*o*-Xylene)	„	11·096	29·177	29·329	37·883	46·852	56·103	65·548	75·110	84·777	94·494	104·23	113·99	123·76	133·50	143·24
1,3- „ (*m*- „)	„	10·926	28·405	28·554	37·008	45·906	55·099	64·492	74·006	83·630	93·307	103·00	112·72	122·45	132·15	141·85
1,4- „ (*p*- „)	„	11·064	28·952	29·104	37·688	46·724	56·060	65·604	75·275	85·058	94·897	104·76	114·64	124·54	134·40	144·27
n-Propylbenzene	C_9H_{12}	9·810	32·810	33·000	43·73	54·94	66·48	78·22	90·09	102·07	114·08	126·1	138·2	150·3	162·3	174·3
Isopropylbenzene (Cumene)	„	9·250	32·738	32·934	43·96	55·46	67·29	79·33	91·48	103·74	116·06	128·4	140·7	153·1	165·4	177·6
1-Methyl-2-ethylbenzene	„	8·092	31·323	31·514	42·26	53·48	65·02	76·78	88·65	100·64	112·67	124·7	136·8	148·9	160·9	173·0
1- „ -3- „	„	7·593	30·217	30·406	41·05	52·20	63·68	75·38	87·20	99·14	111·14	123·2	135·2	147·2	159·2	171·2
1- „ -4- „	„	7·241	30·281	30·472	41·25	52·54	64·16	76·02	88·00	100·10	112·26	124·4	136·6	148·8	161·0	173·2
1,2,3-Trimethylbenzene (Hemimellitene)	„	5·527	29·319	29·513	40·56	52·06	63·91	76·01	88·26	100·63	113·07	125·5	138·0	150·6	163·0	175·5
1,2,4- „ (Pseudocumene)	„	4·468	27·912	28·104	39·02	50·39	62·11	74·07	86·17	98·41	110·71	123·0	135·4	147·8	160·1	172·4
1,3,5- „ (Mesitylene)	„	4·241	28·172	28·369	39·558	51·223	63·237	75·495	87·903	100·443	113·045	125·67	138·32	150·98	163·60	176·23

* See footnote a of Table 3x.

† See footnote b of Table 3x.

‡ See footnote c of Table 3x.

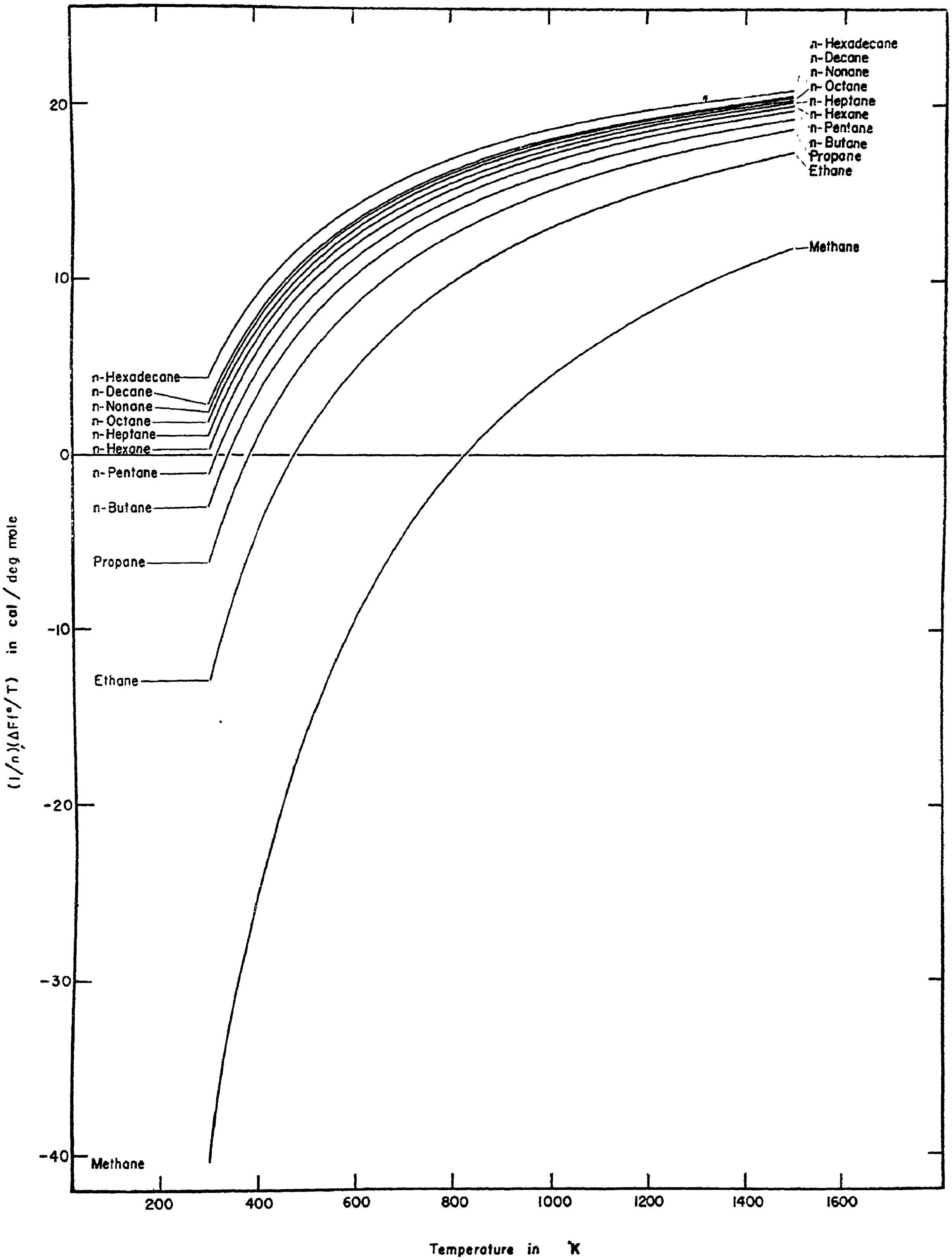


FIG. 2. Thermodynamic stability of the normal paraffin hydrocarbons in the gaseous state as a function of temperature.

The scale of ordinates gives the value of $(1/n)$ $(\Delta Ff^\circ/T)$ in cal/deg. mole, where n is the number of carbon atoms per molecule, T is the absolute temperature in °K., and ΔFf° is the standard free energy of formation of the hydrocarbon from the elements, solid carbon (graphite), and gaseous hydrogen. The scale of abscissae gives the temperature in °K.

This plot shows the thermodynamic stability, per carbon atom, with respect to the elements, of the normal paraffin hydrocarbons in the gaseous state. Points below the zero line indicate that the gaseous hydrocarbon in its standard state has a thermodynamic tendency to be formed from solid (graphite) and gaseous hydrogen in their respective standard states.

II. Reactions involving O_2, H_2, H_2O, C, CO, CO_2, and CH_4

Wagman, Kilpatrick, Taylor, Pitzer, and Rossini [5][1] calculated values for the increment in heat content, the increment in free energy, the logarithm of the equilibrium constant, and the equilibrium constant, to 1,500° K. for the following reactions:

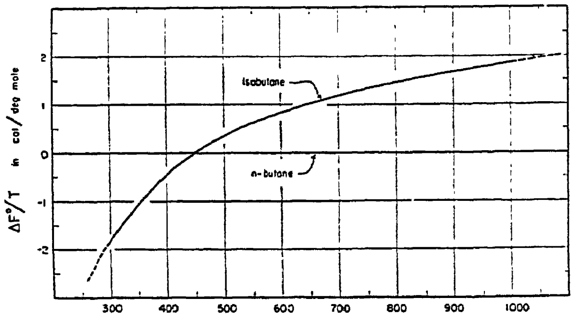


FIG. 3. Free energy of isomerization of the two butanes.

The scale of ordinates gives the value of $\Delta F°/T$, in cal./deg. mole, for the isomerization, $n\text{-}C_4H_{10}(gas) = i\text{-}C_4H_{10}(gas)$. The scale of abscissae gives the temperature in °K.

$$C(solid, graphite)+CO_2(gas) = 2CO(gas) \quad (4)$$
$$C(solid, graphite)+H_2O(gas) = CO(gas)+H_2(gas) \quad (5)$$
$$CO(gas)+\tfrac{1}{2}O_2(gas) = CO_2(gas) \quad (6)$$
$$CO(gas)+H_2O(gas) = CO_2(gas)+H_2(gas) \quad (7)$$
$$CH_4(gas)+\tfrac{1}{2}O_2(gas) = CO(gas)+2H_2(gas) \quad (8)$$
$$CH_4(gas)+CO_2(gas) = 2CO(gas)+2H_2(gas) \quad (9)$$
$$CH_4(gas)+H_2O(gas) = CO(gas)+3H_2(gas) \quad (10)$$
$$CH_4(gas)+2H_2O(gas) = CO_2(gas)+4H_2(gas) \quad (11)$$

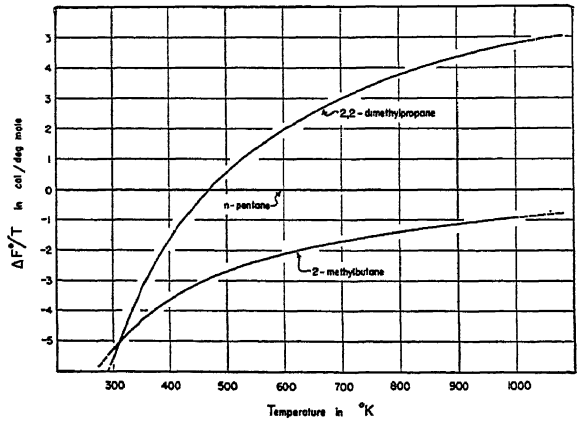


FIG. 4. Free energy of isomerization of the three pentanes.

The scale of ordinates gives the value of $\Delta F°/T$, in cal./deg. mole, for the isomerization, $n\text{-}C_5H_{12}(gas) = i\text{-}C_5H_{12}(gas)$. The scale of abscissae gives the temperature in °K.

Values are presented for the above reactions, to 1,500° K. in Table III for the increment in heat content, $\Delta H°$, and the increment in free energy, ΔF., and in Table IV for the logarithm of the equilibrium constant, $\log_{10}K$, and for the equilibrium constant, K.

In Fig. 1 are plotted the values of the logarithm of the equilibrium constant for these reactions and for the following reaction:

$$C(solid, graphite)+2H_2(gas) = CH_4(gas) \quad (12)$$

III. Paraffin Hydrocarbons

Prosen and Rossini [7], Prosen, Pitzer, and Rossini [6, 8], and Pitzer and Kilpatrick [20] have summarized the results on the thermodynamic properties of the paraffin hydrocarbons.

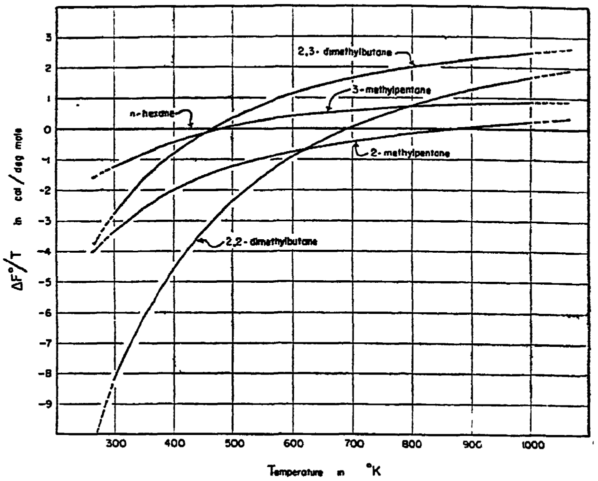


FIG. 5. Free energy of isomerization of the five hexanes.

The scale of ordinates gives the value of $\Delta F°/T$, in cal./deg. mole, for the isomerization, $n\text{-}C_6H_{14}(gas) = i\text{-}C_6H_{14}(gas)$. The scale of abscissae gives the temperature in °K.

Fig. 2 gives a plot which shows the thermodynamic stability, per carbon atom and with respect to the elements solid carbon (graphite) and gaseous hydrogen, of the normal paraffin hydrocarbons in the gaseous state as a function of the temperature.

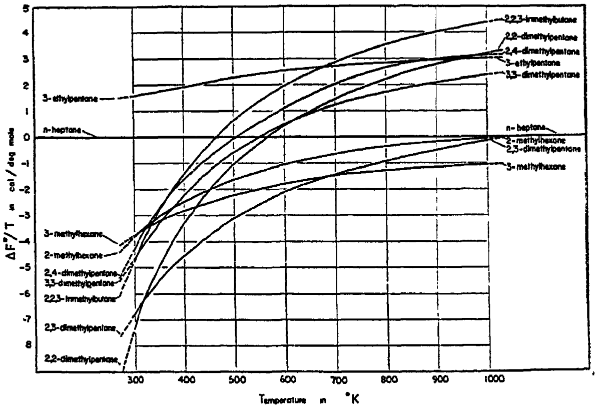


FIG. 6. Free energy of isomerization of the nine heptanes.

The scale of ordinates gives the value of $\Delta F°/T$, in cal./deg. mole, for the isomerization, $n\text{-}C_7H_{16}(gas) = i\text{-}C_7H_{16}(gas)$. The scale of abscissae gives the temperature in °K.

In Figs. 3, 4, 5, 6, and 7 are plotted, respectively for the two butanes, the three pentanes, the five hexanes, the nine heptanes, and the eighteen octanes, the values of $\Delta F./T$, as a function of the temperature T, for the reaction of isomerization in the gaseous state:

$$n\text{-paraffin(gas)} = \text{iso-paraffin(gas)}. \quad (13)$$

From these charts one may see at a glance, for any temperature in the given range and within the limits of uncertainty of the present calculations, which of the isomers, for any

---

[1] The numbers in brackets refer to the publications of the A.P.I. Research Project 44 listed at the end of the paper.

TABLE III

Values of the Heat, $\Delta H°$, and Free Energy, $\Delta F°$, for some Reactions involving O_2, H_2, H_2O, C (Graphite), CO, CO_2, and CH_4

Reaction	Temperature in degrees Kelvin														
	0	298·16	300	400	500	600	700	800	900	1,000	1,100	1,200	1,300	1,400	1,500
	Heat of reaction, $\Delta H°$, in calories per mole														
C (solid, graphite) + CO_2 (gas) = 2CO (gas)	39,565	41,220	41,226	41,435	41,501	41,463	41,353	41,193	40,997	40,781	40,545	40,298	40,031	39,754	39,464
C (solid, graphite) + H_2O (gas) = CO (gas) + H_2 (gas)	29,902	31,382	31,389	31,725	31,981	32,169	32,302	32,391	32,445	32,470	32,474	32,454	32,411	32,348	32,265
CO (gas) + 1/2O_2 (gas) = CO_2 (gas)	−66,767	−67,636	−67,639	−67,752	−67,796	−67,793	−67,760	−67,704	−67,632	−67,550	−67,455	−67,355	−67,243	−67,129	−67,010
CO (gas) + H_2O (gas) = CO_2 (gas) + H_2 (gas)	−9,662	−9,838	−9,837	−9,710	−9,520	−9,294	−9,051	−8,802	−8,552	−8,311	−8,071	−7,844	−7,620	−7,406	−7,199
CH_4 (gas) + 1/2O_2 (gas) = CO (gas) + 2H_2 (gas)	−11,215	−8,527	−8,511	−7,688	−6,993	−6,437	−6,006	−5,689	−5,470	−5,335	−5,262	−5,254	−5,299	−5,379	−5,486
CH_4 (gas) + CO_2 (gas) = 2CO (gas) + 2H_2 (gas)	55,552	59,109	59,128	60,063	60,803	61,356	61,754	62,016	62,162	62,214	62,192	62,100	61,944	61,750	61,524
CH_4 (gas) + H_2O (gas) = CO (gas) + 3H_2 (gas)	45,889	49,271	49,291	50,353	51,283	52,062	52,703	53,214	53,610	53,903	54,122	54,257	54,324	54,344	54,325
CH_4 (gas) + 2H_2O (gas) = CO_2 (gas) + 4H_2 (gas)	36,227	39,433	39,454	40,643	41,763	42,768	43,652	44,412	45,058	45,592	46,051	46,413	46,704	46,938	47,126
	Free energy of reaction, $\Delta F°$, in calories per mole														
C (solid, graphite) + CO_2 (gas) = 2CO (gas)	39,565	28,644	28,567	24,311	20,024	15,727	11,446	7,185	2,946	−1,275	−5,468	−9,645	−13,792	−17,926	−22,034
C (solid, graphite) + H_2O (gas) = CO (gas) + H_2 (gas)	29,902	21,827	21,768	18,509	15,219	11,794	8,387	4,966	1,533	−1,906	−5,354	−8,783	−12,217	−15,646	−19,074
CO (gas) + 1/2O_2 (gas) = CO_2 (gas)	−66,767	−61,452	−61,414	−59,318	−57,208	−55,086	−52,971	−50,862	−48,761	−46,668	−44,584	−42,509	−40,442	−38,382	−36,338
CO (gas) + H_2O (gas) = CO_2 (gas) + H_2 (gas)	−9,662	−6,817	−6,799	−5,802	−4,850	−3,933	−3,059	−2,219	−1,413	−631	+125	862	1,575	2,280	2,960
CH_4 (gas) + 1/2O_2 (gas) = CO (gas) + 2H_2 (gas)	−11,215	−20,668	−20,742	−24,944	−29,344	−33,868	−38,474	−43,130	−47,826	−52,552	−57,272	−62,000	−66,729	−71,450	−76,165
CH_4 (gas) + CO_2 (gas) = 2CO (gas) + 2H_2 (gas)	55,552	40,783	40,672	34,376	27,863	21,218	14,497	7,732	935	−5,884	−12,687	−19,492	−26,287	−33,068	−39,828
CH_4 (gas) + H_2O (gas) = CO (gas) + 3H_2 (gas)	45,889	33,967	33,873	28,573	23,013	17,285	11,437	5,512	−478	−6,517	−12,563	−18,631	−24,713	−30,789	−36,869
CH_4 (gas) + 2H_2O (gas) = CO_2 (gas) + 4H_2 (gas)	36,227	27,150	27,074	22,771	18,163	13,352	8,378	3,293	−1,891	−7,148	−12,438	−17,769	−23,138	−28,509	−33,909

TABLE IV

Values of the Logarithm of the Equilibrium Constant, $\log_{10}K$, and the Equilibrium Constant, K, for some Reactions involving O_2, H_2, H_2O, C (Graphite), CO, CO_2, and CH_4

Reaction	Temperature in degrees Kelvin													
	298·16	*300*	*400*	*500*	*600*	*700*	*800*	*900*	*1,000*	*1,100*	*1,200*	*1,300*	*1,400*	*1,500*
	Logarithm of the equilibrium constant, $\log_{10}K$													
C (solid, graphite)+CO_2 (gas) = 2CO (gas)	−20·99575	−20·81089	−13·28281	−8·75242	−5·72851	−3·57358	−1·96284	−0·71538	+0·27865	1·08638	1·75658	2·31863	2·79835	3·21033
C (solid, graphite)+H_2O (gas) = CO (gas)+H_2 (gas)	−15·99896	−15·85786	−10·11277	−6·65217	−4·29593	−2·61852	−1·35664	−0·37226	+0·41655	1·06373	1·59959	2·05385	2·44243	2·77906
CO (gas)+1/2O_2 (gas) = CO_2 (gas)	+45·04367	44·73973	32·40960	25·00541	20·06491	16·53817	13·89475	11·84070	10·19920	8·85796	7·74189	6·79887	5·99165	5·29440
CO (gas)+H_2O (gas) = CO_2 (gas)+H_2 (gas)	+4·99679	4·95303	3·17004	2·10025	1·43258	0·95506	0·60620	0·34312	0·13790	−0·02484	−0·15699	−0·26478	−0·35592	−0·43127
CH_4 (gas)+1/2O_2 (gas) = CO (gas)+2H_2 (gas)	+15·14943	15·11042	13·62866	12·82615	12·33631	12·01203	11·78248	11·61365	11·48514	11·37881	11·29165	11·21808	11·15376	11·09715
CH_4 (gas)+CO_2 (gas) = 2CO (gas)+2H_2 (gas)	−29·89351	−29·62931	−18·78203	−12·17882	−7·72859	−4·52613	−2·11227	−0·22705	+1·28594	2·52066	3·54995	4·41921	5·16211	5·80289
CH_4 (gas)+H_2O (gas) = CO (gas)+3H_2 (gas)	−24·89745	−24·67628	−15·61144	−10·05889	−6·29601	−3·57077	−1·50580	+0·11607	1·42428	2·49602	3·39314	4·15460	4·80634	5·37177
CH_4 (gas)+2H_2O (gas) = CO_2 (gas)+4H_2 (gas)	−19·90067	−19·72325	−12·44091	−7·93898	−4·86343	−2·61571	−0·89960	+0·45919	1·56218	2·47118	3·23615	3·88982	4·45042	4·94050
	Equilibrium constant, K													
C (solid, graphite)+CO_2 (gas) = 2CO (gas)	$1{\cdot}012\times10^{-21}$	$1{\cdot}546\times10^{-21}$	$5{\cdot}214\times10^{-14}$	$1{\cdot}768\times10^{-9}$	$1{\cdot}868\times10^{-6}$	$2{\cdot}669\times10^{-4}$	$1{\cdot}098\times10^{-2}$	0·1926	1·900	12·20	57·09	$2{\cdot}083\times10^{2}$	$6{\cdot}286\times10^{2}$	$1{\cdot}623\times10^{3}$
C (solid, graphite)+H_2O (gas) = CO (gas)+H_2 (gas)	$1{\cdot}002\times10^{-16}$	$1{\cdot}387\times10^{-16}$	$7{\cdot}713\times10^{-11}$	$2{\cdot}228\times10^{-7}$	$5{\cdot}059\times10^{-5}$	$2{\cdot}407\times10^{-3}$	$4{\cdot}399\times10^{-2}$	0·4244	2·609	11·58	39·77	$1{\cdot}135\times10^{2}$	$2{\cdot}770\times10^{2}$	$6{\cdot}013\times10^{2}$
CO (gas)+1/2O_2 (gas) = CO_2 (gas)	$1{\cdot}106\times10^{45}$	$5{\cdot}492\times10^{44}$	$2{\cdot}568\times10^{32}$	$1{\cdot}013\times10^{25}$	$1{\cdot}161\times10^{20}$	$3{\cdot}453\times10^{16}$	$7{\cdot}848\times10^{13}$	$6{\cdot}930\times10^{11}$	$1{\cdot}582\times10^{10}$	$7{\cdot}210\times10^{8}$	$5{\cdot}519\times10^{7}$	$6{\cdot}293\times10^{6}$	$9{\cdot}810\times10^{5}$	$1{\cdot}970\times10^{5}$
CO (gas)+H_2O (gas) = CO_2 (gas)+H_2 (gas)	$9{\cdot}926\times10^{4}$	$8{\cdot}975\times10^{4}$	$1{\cdot}479\times10^{3}$	$1{\cdot}260\times10^{2}$	27·08	9·017	4·038	2·204	1·374	0·9444	0·6966	0·5435	0·4406	0·3704
CH_4 (gas)+1/2O_2 (gas) = CO (gas)+2H_2 (gas)	$1{\cdot}411\times10^{15}$	$1{\cdot}290\times10^{15}$	$4{\cdot}253\times10^{13}$	$6{\cdot}710\times10^{12}$	$2{\cdot}169\times10^{12}$	$1{\cdot}028\times10^{12}$	$6{\cdot}060\times10^{11}$	$4{\cdot}108\times10^{11}$	$3{\cdot}056\times10^{11}$	$2{\cdot}392\times10^{11}$	$1{\cdot}957\times10^{11}$	$1{\cdot}652\times10^{11}$	$1{\cdot}425\times10^{11}$	$1{\cdot}251\times10^{11}$
CH_4 (gas)+CO_2 (gas) = 2CO (gas)+2H_2 (gas)	$1{\cdot}278\times10^{-30}$	$2{\cdot}348\times10^{-30}$	$1{\cdot}625\times10^{-19}$	$6{\cdot}625\times10^{-13}$	$1{\cdot}868\times10^{-8}$	$2{\cdot}978\times10^{-5}$	$7{\cdot}722\times10^{-3}$	0·5929	19·32	$3{\cdot}316\times10^{2}$	$3{\cdot}548\times10^{3}$	$2{\cdot}626\times10^{4}$	$1{\cdot}452\times10^{5}$	$6{\cdot}352\times10^{5}$
CH_4 (gas)+H_2O (gas) = CO (gas)+3H_2 (gas)	$1{\cdot}266\times10^{-25}$	$2{\cdot}107\times10^{-25}$	$2{\cdot}447\times10^{-16}$	$8{\cdot}732\times10^{-11}$	$5{\cdot}058\times10^{-7}$	$2{\cdot}687\times10^{-4}$	$3{\cdot}120\times10^{-2}$	1·306	26·56	$3{\cdot}133\times10^{2}$	$2{\cdot}473\times10^{3}$	$1{\cdot}428\times10^{4}$	$6{\cdot}402\times10^{4}$	$2{\cdot}354\times10^{5}$
CH_4 (gas)+2H_2O (gas) = CO_2 (gas)+4H_2 (gas)	$1{\cdot}257\times10^{-20}$	$1{\cdot}891\times10^{-20}$	$3{\cdot}623\times10^{-13}$	$1{\cdot}151\times10^{-8}$	$1{\cdot}369\times10^{-5}$	$2{\cdot}423\times10^{-3}$	0·1260	2·879	36·49	$2{\cdot}959\times10^{2}$	$1{\cdot}723\times10^{3}$	$7{\cdot}759\times10^{3}$	$2{\cdot}821\times10^{4}$	$8{\cdot}720\times10^{4}$

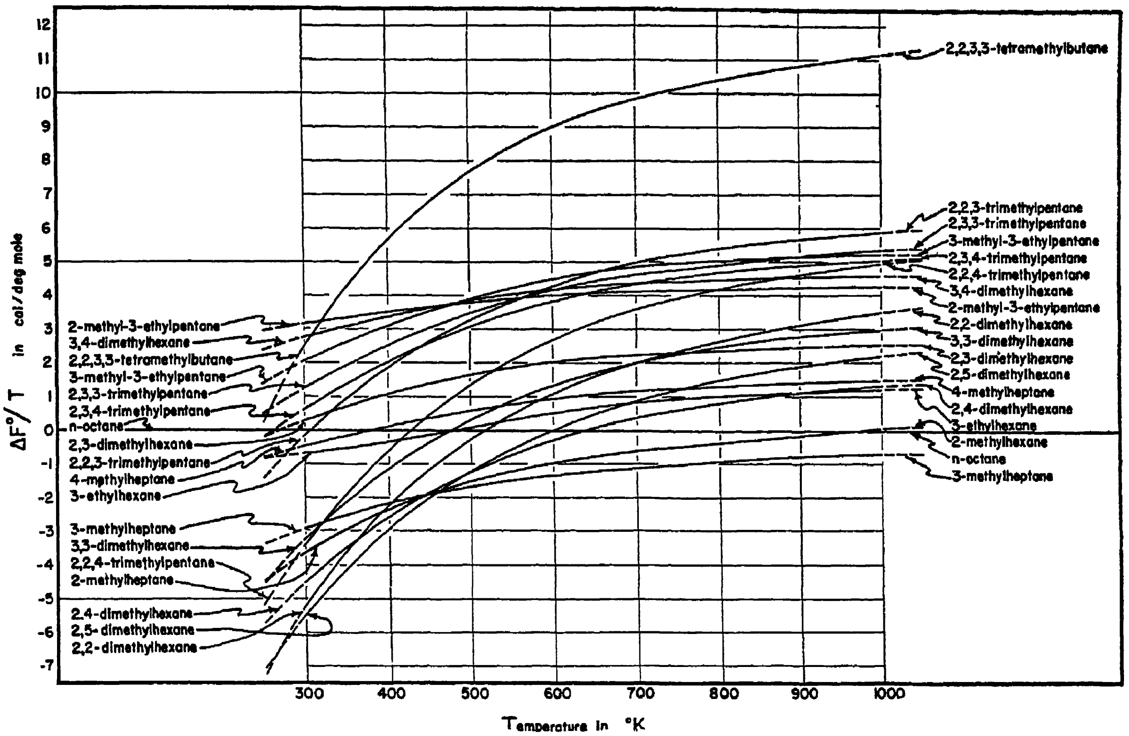


FIG. 7. Free energy of isomerization of the eighteen octanes.

The scale of ordinates gives the value of Δ *F.*/*T*, in cal./deg. mole, for the isomerization, n-C_8H_{18} (gas) = i-C_8H_{18} (gas). The scale of abscissae gives the temperature in °K.

given number of carbon atoms, is thermodynamically the most stable (lowest value of Δ *F.*/*T*), which is the least stable (highest value of Δ *F.*/*T*), and the order of stability of the other isomers. From the assigned uncertainties [6, 8], it follows that those isomers having at some given temperature values of Δ *F.*/*T* that differ by less than the uncertainty are ones for which the exact order of stability cannot be stated since the values overlap. In such cases the amounts present at equilibrium will be substantially equal.

In Figs. 8, 9, 10, 11, and 12 are plotted, as a function of the temperature, the amounts, in mole fraction, of each of the isomers present at equilibrium with all its other isomers in the gas phase, respectively for the two butanes, the three pentanes, the five hexanes, the nine heptanes, and the eighteen octanes. The vertical width of each band gives the mole fraction for that isomer at the selected temperature. The mole fractions of the several isomers are plotted additively, so that their sum is unity at all temperatures.

With regard to the thermodynamic stability of the isomers, among the butanes, pentanes, hexanes, heptanes, and octanes, respectively, the following general conclusions may be drawn:

(*a*) At 25° C. the normal isomer is among the isomers of lesser stability. Relative to the other isomers, the normal isomer increases in stability with increase in temperature, and at 1,000° K. is among the most stable of the isomers.

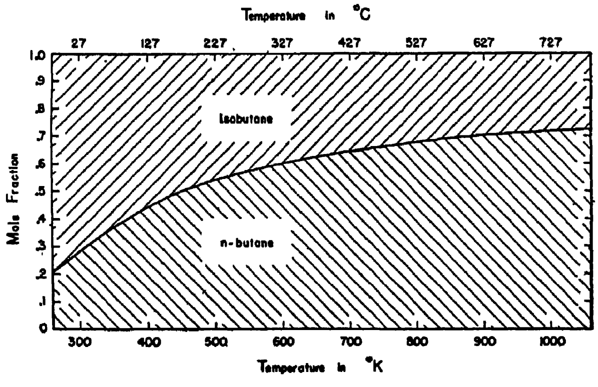


FIG. 8. Equilibrium concentrations of the two butanes.

The scale of ordinates measures the amount in mole fraction, and the scale of abscissae gives the temperature in °K. and °C. The vertical width of a band at a given temperature measures the mole fraction of the given isomer present at equilibrium with all of its other isomers, in the gas phase.

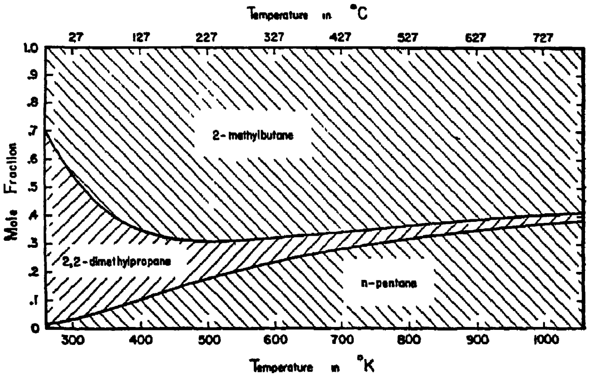


FIG. 9. Equilibrium concentrations of the three pentanes.

The scale of ordinates measures the amount in mole fraction, and the scale of abscissae gives the temperature in °K. and °C. The vertical width of a band at a given temperature measures the mole fraction of the given isomer present at equilibrium with all of its other isomers, in the gas phase.

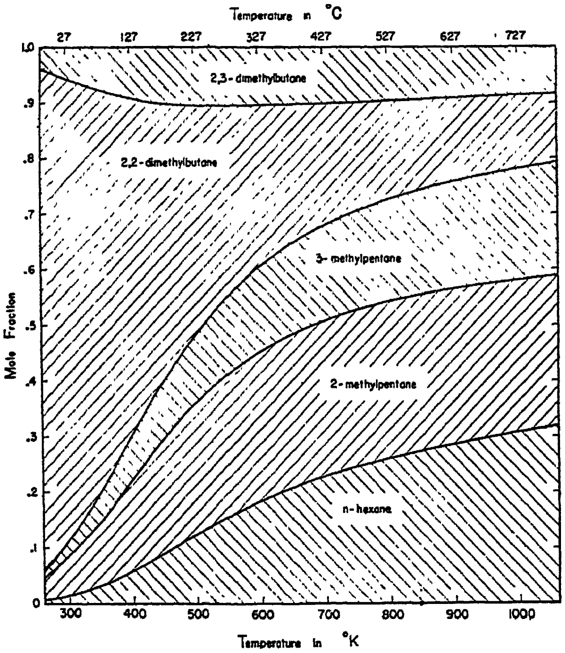


FIG. 10. Equilibrium concentrations of the five hexanes.

The scale of ordinates measures the amount in mole fraction, and the scale of abscissae gives the temperature in °K. and °C. The vertical width of a band at a given temperature measures the mole fraction of the given isomer present at equilibrium with all of its isomers, in the gas phase.

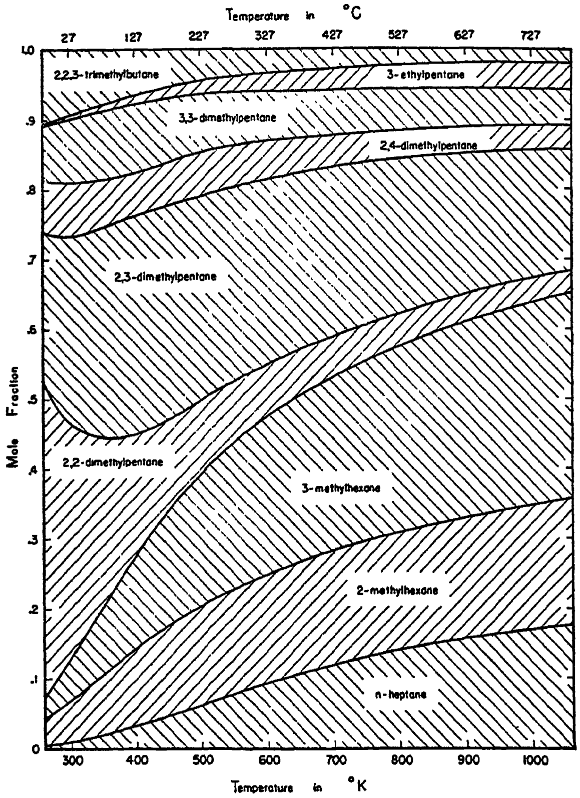


FIG. 11. Equilibrium concentrations of the nine heptanes.

The scale of ordinates measures the amount in mole fraction, and the scale of abscissae gives the temperature in °K. and °C. The vertical width of a band at a given temperature measures the mole fraction of the given isomer present at equilibrium with all of its other isomers, in the gas phase.

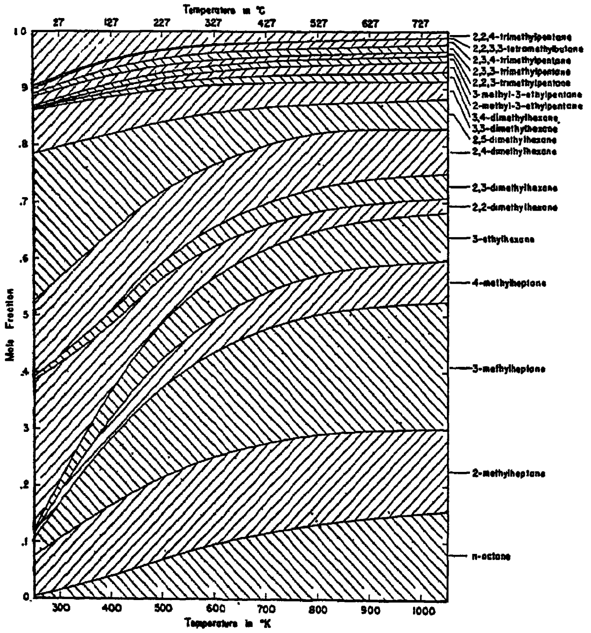


FIG. 12. Equilibrium concentrations of the eighteen octanes.

The scale of ordinates measures the amount in mole fraction, and the scale of abscissae gives the temperature in °K. and °C. The vertical width of a band at a given temperature measures the mole fraction of the given isomer present at equilibrium with all of its other isomers, in the gas phase.

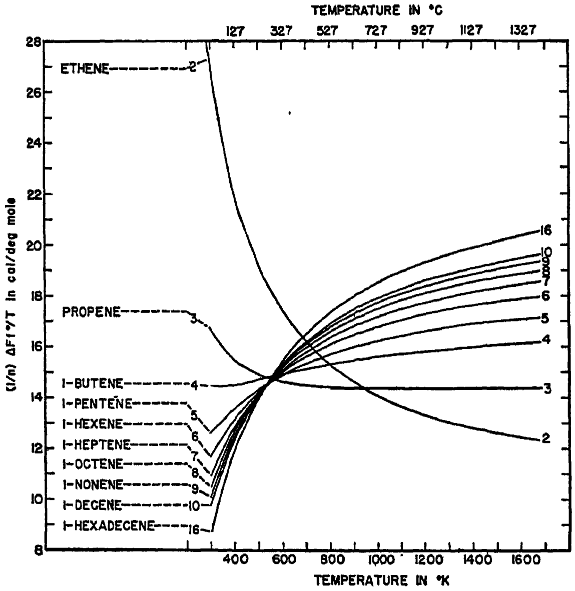


FIG. 13. Thermodynamic stability of the 1-alkene hydrocarbons in the gaseous state as a function of temperature.

The scale of ordinates gives the value of $(1/n)$ $(\Delta\, Ff./T)$ in calories per degree mole, where n is the number of carbon atoms per molecule, T is the absolute temperature in °K., and $\Delta\, Ff°$ is the standard free energy of formation of the hydrocarbon from the elements, solid carbon (graphite) and gaseous hydrogen. The scale of abscissae gives the temperature in °K. and °C.

(*b*) At 25° C. the 2,2-dimethyl isomer is among the most stable of the isomers, but it rapidly becomes less stable with increasing temperature and at 1,000° K. is among the least stable of the isomers.

(*c*) The more highly branched isomers are among the least stable at the higher temperatures.

IV. Mono-olefine Hydrocarbons

Kilpatrick, Prosen, Pitzer, and Rossini [15], Prosen and Rossini [13], and Kilpatrick and Pitzer [18] have summarized the results on the thermodynamic properties of the mono-olefine hydrocarbons.

Fig. 13 shows the thermodynamic stability of the 1-alkenes in the gaseous state as a function of temperature, per carbon atom and with respect to the elements solid carbon (graphite) and gaseous hydrogen. This plot for the 1-alkenes may be compared to the corresponding one for the normal paraffins in Fig. 2.

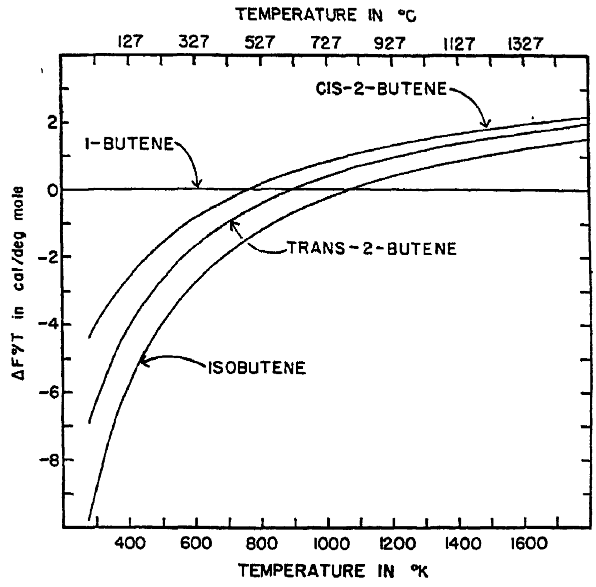


FIG. 14. Free energy of isomerization of the four butenes.

The scale of ordinates gives the value of $\Delta F./T$, in cal./deg. mole, for the isomerization of 1-butene into the other isomers, in the gaseous state, as indicated. The scale of abscissae gives the temperature in °K. and °C.

In Figs. 14, 15, and 16 are plotted, as a function of the temperature T, respectively for the four butenes, the six pentenes, and the seventeen hexenes, the values of $\Delta F./T$ for the reaction of isomerization in the gaseous state:

$$\text{1-alkene, normal (gas)} = \text{isomeric alkene (gas)}. \qquad (14)$$

From these charts one may see at a glance, for any temperature in the given range and within the limits of uncertainty of the calculations, which of the isomers is thermodynamically most stable (lowest value of $\Delta F./T$) and which is the least stable (highest value of $\Delta F./T$). These plots may be compared with the corresponding ones for the butanes, pentanes, hexanes, heptanes, and octanes in Figs. 3, 4, 5, 6, and 7.

In Figs. 17, 18, and 19 are plotted, as a function of temperature, respectively for the four butenes, six pentenes, and seventeen hexenes, the amounts, in mole fraction, of each of the isomers present at equilibrium with its other alkene isomers in the gas phase. The vertical width of each band gives the mole fraction for that isomer at the selected temperature. The mole fractions of the several isomers are plotted additively, so that their sum is unity at all temperatures.

In Fig. 20 are plotted, as a function of the temperature, values of the logarithm of the equilibrium constant for the reaction of hydrogenation of a given 1-alkene to the corresponding normal paraffin, in the gaseous state:

$$\text{1-alkene (gas)} + H_2\text{(gas)} = n\text{-paraffin (gas)}. \qquad (15)$$

The curves show the change in the value of the logarithm of the equilibrium constant of hydrogenation with increase in the number of carbon atoms in the molecule.

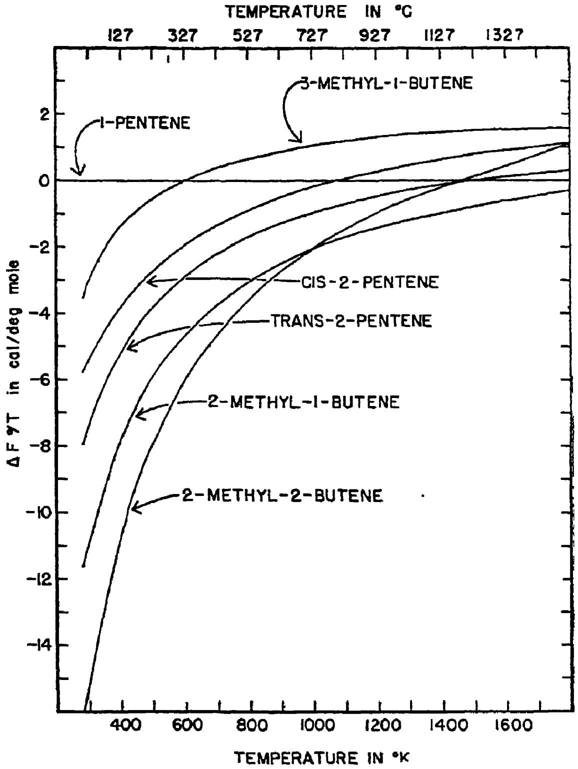


FIG. 15. Free energy of isomerization of the six pentenes.

The scale of ordinates gives the value of $\Delta F./T$, in cal./deg. mole, for the isomerization of 1-pentene into the other isomers, in the gaseous state, as indicated. The scale of abscissae gives the temperature in °K. and °C.

Table V gives the numerical values of the equilibrium constant, and of its logarithm, for these reactions of hydrogenation.

Table VI presents numerical values of the equilibrium constant, and of its logarithm, for the following reactions of dimerization:

$$2C_2H_4\text{(ethylene, gas)} = C_4H_8\text{(1-butene, gas)} \qquad (16)$$
$$2C_3H_6\text{(propylene, gas)} = C_6H_{12}\text{(1-hexene, gas)} \qquad (17)$$
$$2C_4H_8\text{(1-butene, gas)} = C_8H_{16}\text{(1-octene, gas)} \qquad (18)$$
$$2C_5H_{10}\text{(1-pentene, gas)} = C_{10}H_{20}\text{(1-decene, gas)} \qquad (19)$$
$$2C_nH_{2n}\text{(1-alkene, normal, gas)} = C_{2n}H_{4n}\text{(1-alkene, normal, gas)};\ n > 5. \qquad (20)$$

In Fig. 21 are plotted, as a function of temperature, values of the logarithm of the equilibrium constant for these reactions of dimerization.

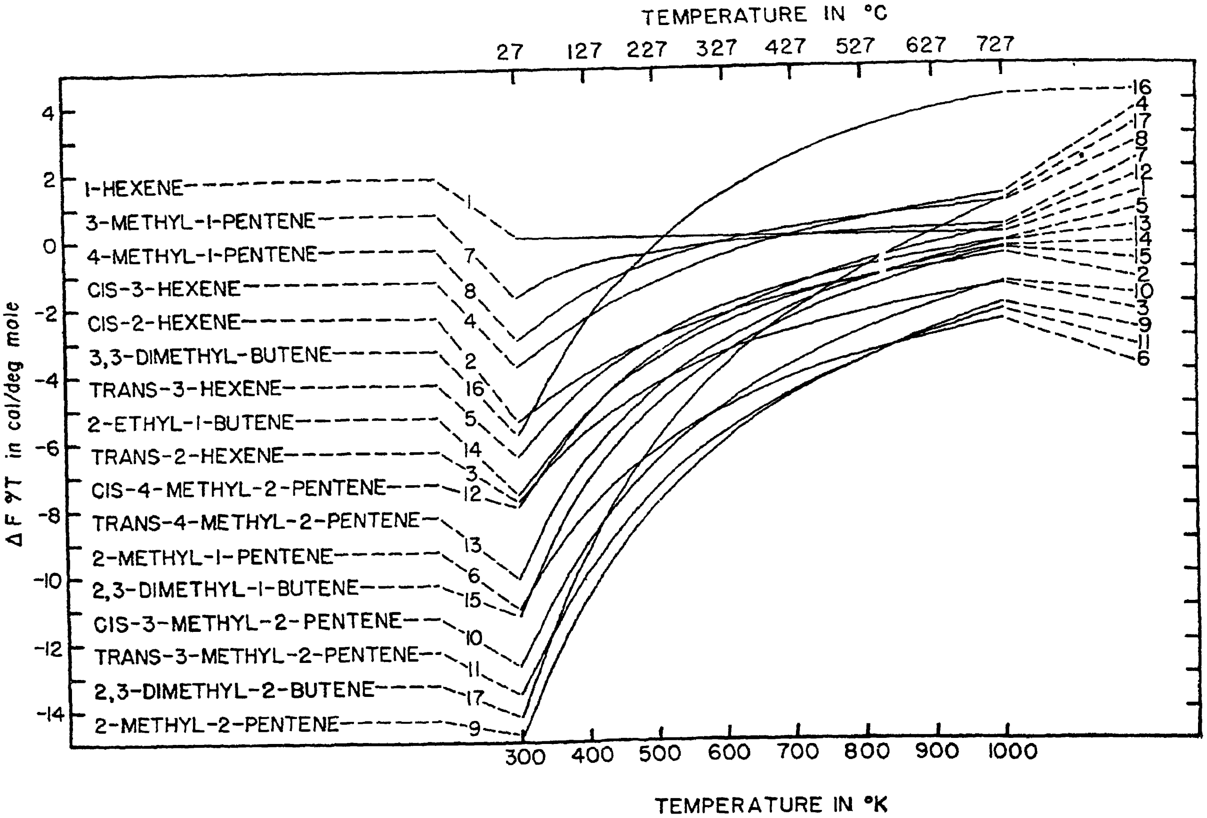


FIG. 16. Free energy of isomerization of the seventeen hexenes.

The scale of ordinates gives the value of Δ *F./T*, in cal./deg. mole, for the isomerization of 1-hexene into the other isomers, in the gaseous state, as indicated. The scale of abscissae gives the temperature in °K. and °C.

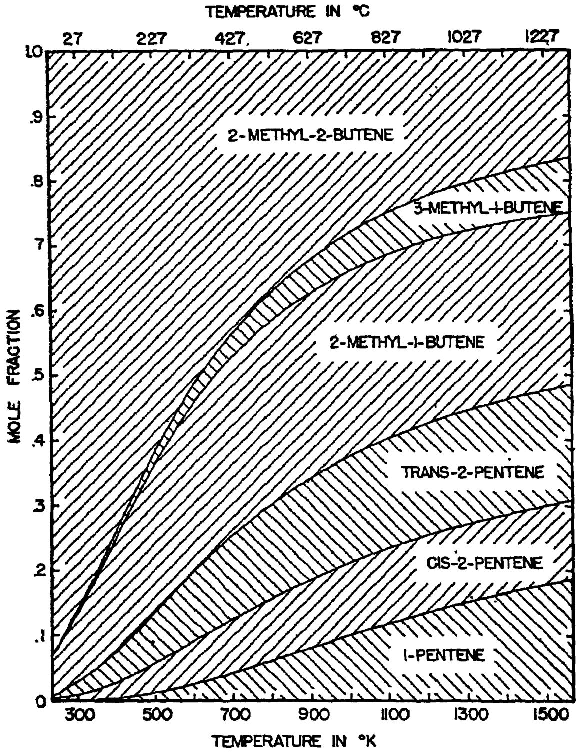


FIG. 17. Equilibrium concentrations of the four butenes.

The scale of ordinates measures the amount in mole fraction, and the scale of abscissae gives the temperature in °K. and °C. The vertical width of a band at a given temperature measures the mole fraction of the given isomer present when at equilibrium with all of its other isomers, in the gas phase.

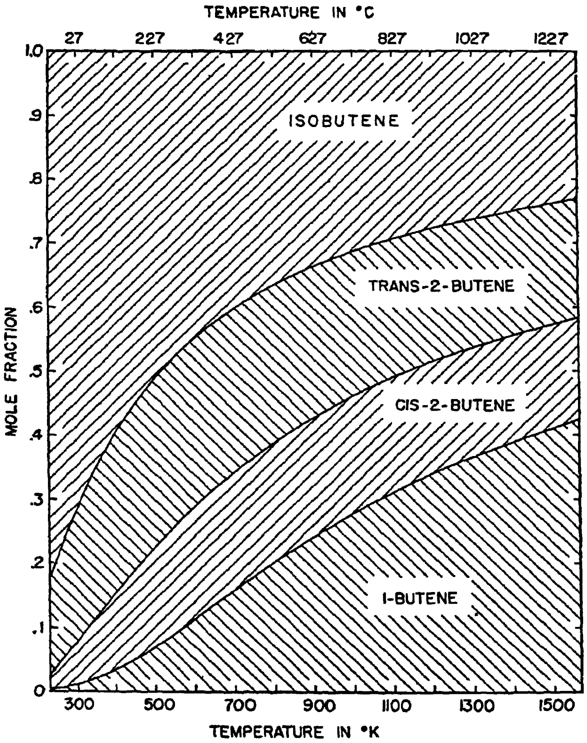


FIG. 18. Equilibrium concentrations of the six pentenes.

The scale of ordinates measures the amount in mole fraction, and the scale of abscissae gives the temperature in °K. and °C. The vertical width of a band at a given temperature measures the mole fraction of the given isomer present when at equilibrium with all of its other isomers, in the gas phase.

TABLE V

Equilibrium Constant, and its Logarithm, for the Reaction of Hydrogenation of 1-Alkenes to n-Paraffins

Reaction	Temperature in °K.													
	298·16	300	400	500	600	700	800	900	1,000	1,100	1,200	1,300	1,400	1,500
1-Alkene (gas)+H_2 (gas) = n-paraffin (gas)	*Logarithm of the equilibrium constant, $\log_{10} K$*													
C_2H_4 (gas)+H_2 (gas) = C_2H_6 (gas)	17·6958	17·5494	11·5404	7·9014	5·4444	3·6778	2·3423	1·2992	0·4634	−0·2229	−0·7937	−1·2766	−1·6897	−2·0495
C_3H_6 (gas)+H_2 (gas) = C_3H_8 (gas)	15·1025	15·0014	9·5170	6·2154	3·9906	2·3935	1·1911	0·2547	−0·4930	−1·1044	−1·6136	−2·0430	−2·4116	−2·7382
C_4H_8 (gas)+H_2 (gas) = C_4H_{10} (gas)	15·3715	15·2364	9·7090	6·3650	4·1017	2·4706	1·2443	0·2890	−0·4758	−1·1039	−1·6302	−2·0772	−2·4581	−2·7908
C_5H_{10} (gas)+H_2 (gas) = C_5H_{12} (gas)	15·2070	15·0725	9·5615	6·2095	3·9550	2·3313	1·1050	0·1492	−0·6177	−1·2431	−1·7653	−2·2042	−2·5838	−2·9200
C_6H_{12} (gas)+H_2 (gas) = C_6H_{14} (gas)	15·2121	15·0748	9·5646	6·2247	3·9683	2·3428	1·1243	0·1639	−0·6017	−1·2271	−1·7490	−2·1890	−2·5712	−2·9090
C_nH_{2n} (gas)+H_2 (gas) = C_nH_{2n+2} (gas); $n>6$	15·2090	15·0773	9·5649	6·2228	3·9669	2·3402	1·1210	0·1635	−0·6008	−1·2284	−1·7475	−2·1889	−2·5706	−2·9101
	Equilibrium constant, K													
C_2H_4 (gas)+H_2 (gas) = C_2H_6 (gas)	$4·97\times10^{17}$	$3·54\times10^{17}$	$3·47\times10^{11}$	$7·96\times10^{7}$	$2·78\times10^{5}$	$4·76\times10^{3}$	$2·20\times10^{2}$	19·9	2·90	$5·98\times10^{-1}$	$1·61\times10^{-1}$	$5·28\times10^{-2}$	$2·04\times10^{-2}$	$8·91\times10^{-3}$
C_3H_6 (gas)+H_2 (gas) = C_3H_8 (gas)	$1·27\times10^{15}$	$1·00\times10^{15}$	$3·29\times10^{9}$	$1·64\times10^{6}$	$9·78\times10^{3}$	$2·47\times10^{2}$	$1·55\times10^{1}$	1·80	0·321	$7·86\times10^{-2}$	$2·44\times10^{-2}$	$9·06\times10^{-3}$	$3·88\times10^{-3}$	$1·83\times10^{-3}$
C_4H_8 (gas)+H_2 (gas) = C_4H_{10} (gas)	$2·35\times10^{15}$	$1·72\times10^{15}$	$5·12\times10^{9}$	$2·32\times10^{6}$	$1·26\times10^{4}$	$2·95\times10^{2}$	$1·75\times10^{1}$	1·95	0·334	$7·87\times10^{-2}$	$2·34\times10^{-2}$	$8·37\times10^{-3}$	$3·48\times10^{-3}$	$1·62\times10^{-3}$
C_5H_{10} (gas)+H_2 (gas) = C_5H_{12} (gas)	$1·61\times10^{15}$	$1·18\times10^{15}$	$3·64\times10^{9}$	$1·62\times10^{6}$	$9·02\times10^{3}$	$2·14\times10^{2}$	$1·27\times10^{1}$	1·41	0·241	$5·72\times10^{-2}$	$1·72\times10^{-2}$	$6·25\times10^{-3}$	$2·61\times10^{-3}$	$1·51\times10^{-3}$
C_6H_{12} (gas)+H_2 (gas) = C_6H_{14} (gas)	$1·63\times10^{15}$	$1·19\times10^{15}$	$3·67\times10^{9}$	$1·68\times10^{6}$	$9·29\times10^{3}$	$2·20\times10^{2}$	$1·33\times10^{1}$	1·46	0·250	$5·93\times10^{-2}$	$1·78\times10^{-2}$	$6·47\times10^{-3}$	$2·69\times10^{-3}$	$1·23\times10^{-3}$
C_nH_{2n} (gas)+H_2 (gas) = C_nH_{2n+2} (gas); $n>6$	$1·63\times10^{15}$	$1·19\times10^{15}$	$3·67\times10^{9}$	$1·67\times10^{6}$	$9·27\times10^{3}$	$2·19\times10^{2}$	$1·32\times10^{1}$	1·46	0·251	$5·91\times10^{-2}$	$1·79\times10^{-2}$	$6·47\times10^{-3}$	$2·69\times10^{-3}$	$1·23\times10^{-3}$

TABLE VI

Equilibrium Constant, and its Logarithm, for the Reaction of Dimerization of Normal 1-Alkenes to Normal 1-Alkenes

Reaction	Temperature in °K.													
	298·16	300	400	500	600	700	800	900	1,000	1,100	1,200	1,300	1,400	1,500
	Logarithm of the equilibrium constant, $\log_{10} K$													
$2C_2H_4$ (ethylene, gas) = C_4H_8 (1-butene, gas)	11·249	11·139	6·636	3·960	2·180	0·919	−0·020	−0·745	−1·319	−1·787	−2·172	−2·495	−2·768	−3·004
$2C_3H_6$ (propylene, gas) = C_6H_{12} (1-hexene, gas)	6·650	6·559	2·976	0·857	−0·546	−1·534	−2·268	−2·822	−3·263	−3·619	−3·922	−4·176	−4·387	−4·564
$2C_4H_8$ (1-butene, gas) = C_8H_{16} (1-octene, gas)	6·996	6·899	3·191	1·005	−0·445	−1·472	−2·230	−2·811	−3·272	−3·643	−3·954	−4·218	−4·440	−4·637
$2C_5H_{10}$ (1-pentene, gas) = $C_{10}H_{20}$ (1-decene, gas)	6·291	6·200	2·617	0·495	−0·905	−1·891	−2·625	−3·191	−3·639	−3·992	−4·287	−4·529	−4·746	−4·951
$2C_nH_{2n}$ (1-alkene, normal, gas) = $C_{2n}H_{4n}$ (1-alkene, normal, gas); $n>5$	6·251	6·161	2·590	0·491	−0·904	−1·892	−2·611	−3·182	−3·626	−3·970	−4·263	−4·509	−4·730	−4·940
	Equilibrium constant, K													
$2C_2H_4$ (ethylene, gas) = C_4H_8 (1-butene, gas)	$1·77\times10^{11}$	$1·38\times10^{11}$	$4·33\times10^{6}$	$9·12\times10^{3}$	$1·51\times10^{2}$	8·30	0·955	0·180	$4·80\times10^{-2}$	$1·63\times10^{-2}$	$6·73\times10^{-3}$	$3·20\times10^{-3}$	$1·71\times10^{-3}$	$9·91\times10^{-4}$
$2C_3H_6$ (propylene, gas) = C_6H_{12} (1-hexene, gas)	$4·46\times10^{6}$	$3·62\times10^{6}$	$9·46\times10^{2}$	7·19	0·284	$2·92\times10^{-2}$	$5·40\times10^{-3}$	$1·51\times10^{-3}$	$5·64\times10^{-4}$	$2·40\times10^{-4}$	$1·20\times10^{-4}$	$6·67\times10^{-5}$	$4·10\times10^{-5}$	$2·73\times10^{-5}$
$2C_4H_8$ (1-butene, gas) = C_8H_{16} (1-octene, gas)	$9·91\times10^{6}$	$7·93\times10^{6}$	$1·55\times10^{3}$	10·1	0·359	$3·37\times10^{-2}$	$5·89\times10^{-3}$	$1·55\times10^{-3}$	$5·35\times10^{-4}$	$2·28\times10^{-4}$	$1·11\times10^{-4}$	$6·05\times10^{-5}$	$3·63\times10^{-5}$	$2·31\times10^{-5}$
$2C_5H_{10}$ (1-pentene, gas) = $C_{10}H_{20}$ (1-decene, gas)	$1·95\times10^{6}$	$1·59\times10^{6}$	$4·14\times10^{2}$	3·13	0·125	$1·29\times10^{-2}$	$2·37\times10^{-3}$	$6·44\times10^{-4}$	$2·30\times10^{-4}$	$1·02\times10^{-4}$	$5·16\times10^{-5}$	$2·96\times10^{-5}$	$1·80\times10^{-5}$	$1·12\times10^{-5}$
$2C_nH_{2n}$ (1-alkene, normal, gas) = $C_{2n}H_{4n}$ (1-alkene, normal, gas); $n>5$	$1·78\times10^{6}$	$1·45\times10^{6}$	$3·90\times10^{2}$	3·10	0·125	$1·28\times10^{-2}$	$2·45\times10^{-3}$	$6·58\times10^{-4}$	$2·37\times10^{-4}$	$1·07\times10^{-4}$	$5·46\times10^{-5}$	$3·10\times10^{-5}$	$1·86\times10^{-5}$	$1·15\times10^{-5}$

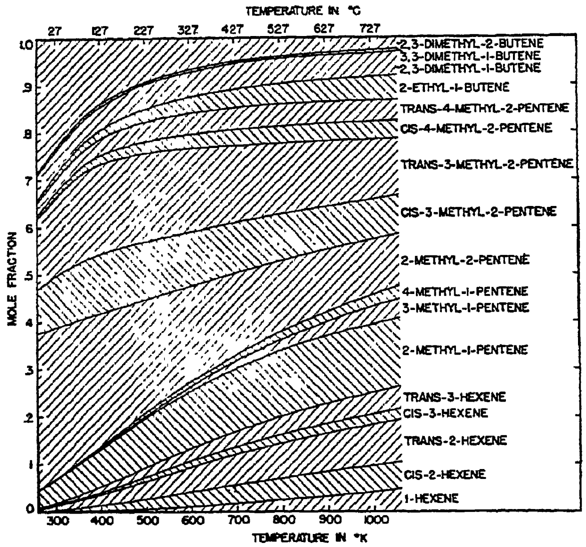


FIG. 19. Equilibrium concentrations of the seventeen hexenes.

The scale of ordinates measures the amount in mole fraction, and the scale of abscissae gives the temperature in °K. and °C. The vertical width of a band at a given temperature measures the mole fraction of the given isomer present when at equilibrium with all of its other isomers, in the gas phase.

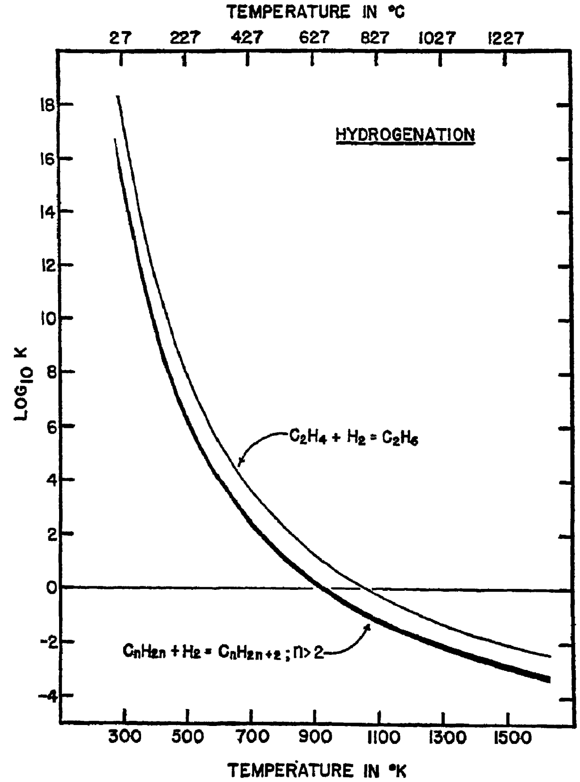


FIG. 20. Logarithm of the equilibrium constant for the reaction of hydrogenation of 1-alkenes to *n*-paraffins.

The scale of ordinates gives the value of the logarithm (to the base 10) of the equilibrium constant for the reaction of hydrogenation of a given 1-alkene to the corresponding normal paraffin, in the gaseous state. The scale of abscissae gives the temperature in °K. and °C. The values calculated for propylene, 1-butene, and the higher 1-alkenes all fall within the width of the heavy line indicated. The corresponding numerical values are given in Table V.

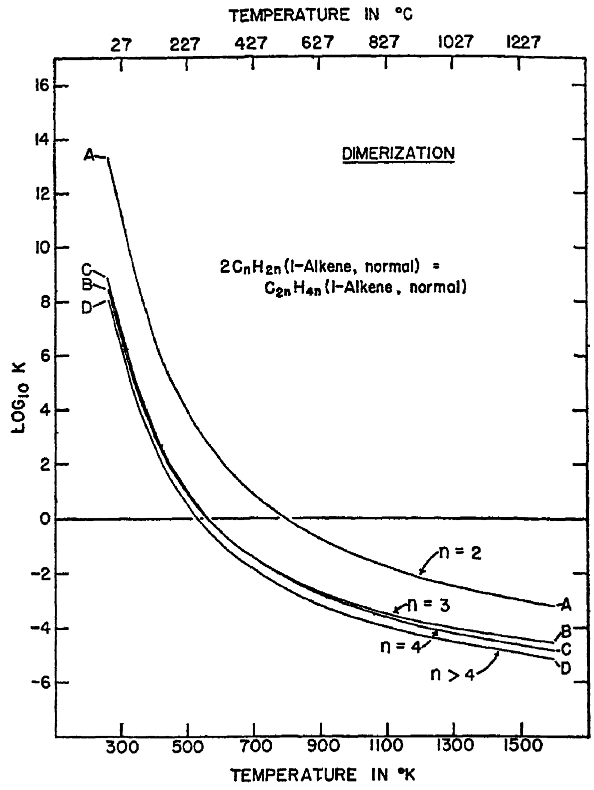


FIG. 21. Logarithm of the equilibrium constant for some reactions of dimerization.

The scale of ordinates gives the value of the logarithm (to the base 10) of the equilibrium constant for some reactions of dimerization of 1-alkenes to 1-alkenes, in the gaseous state. The scale of abscissae gives the temperature in °K. and °C. The lowest curve shown is that for 1-pentene and higher 1-alkenes. The corresponding numerical values are given in Table VI.

Table VII presents numerical values of the equilibrium constant, and of its logarithm, for the following reactions of alkylation, involving the addition of a paraffin to a mono-olefine:

ethylene (gas) + isobutane (gas)
= 2,3-dimethylbutane (gas) (21)
propylene (gas) + isobutane (gas)
= 2,3-dimethylbutane (gas) (22)
isobutene (gas) + isobutane (gas)
= 2,2,4-trimethylpentane (gas) (23)
2-methyl-2-butene (gas) + isobutane (gas)
= 2,2,5-trimethylhexane (gas). (24)

In Fig. 22 are plotted, as a function of temperature, values of the logarithm of the equilibrium constant for the above reactions of alkylation.

V. Acetylene Hydrocarbons

Wagman, Kilpatrick, Pitzer, and Rossini [12] have summarized the results on the thermodynamic properties of the acetylene hydrocarbons.

Fig. 23 shows the thermodynamic stability of the 1-alkynes in the gaseous state as a function of the temperature, in the form of a plot of the standard free energy of formation, per carbon atom, divided by the absolute temperature. This plot may be compared with the corre-

TABLE VII

Equilibrium Constant, and its Logarithm, for some Reactions of Alkylation (Addition of Olefine to Paraffin)

Reaction	*Temperature in °K.*								
Mono-olefine (gas)+isobutane (gas) = isoparaffin (gas)	*298·16*	*300*	*400*	*500*	*600*	*700*	*800*	*900*	*1,000*
	Logarithm of the equilibrium constant, $\log_{10} K$								
Ethylene (gas)+isobutane (gas) = 2,3-dimethylbutane (gas)	9·321	9·214	4·993	2·475	0·793	−0·393	−1·264	−1·925	−2·434
Propylene (gas)+isobutane (gas) = 2,3-dimethylpentane (gas)	7·703	7·611	3·832	1·564	0·045	−1·036	−1·828	−2·424	−2·877
Isobutene (gas)+isobutane (gas) = 2,2,4-trimethylpentane (gas)	5·240	5·156	1·807	−0·210	−1·560	−2·507	−3·177	−3·678	−4·073
2-Methyl-2-butene (gas)+isobutane (gas) = 2,2,5-trimethylhexane (gas)	3·710	3·633	0·647	−1·128	−2·313	−3·134	−3·700	−4·120	−4·458
	Equilibrium constant, K								
Ethylene (gas)+isobutane (gas) = 2,3-dimethylbutane (gas)	$2·09 \times 10^{9}$	$1·64 \times 10^{9}$	$9·84 \times 10^{4}$	$2·99 \times 10^{2}$	6·21	0·405	$5·45 \times 10^{-2}$	$1·19 \times 10^{-2}$	$3·68 \times 10^{-3}$
Propylene (gas)+isobutane (gas) = 2,3-dimethylpentane (gas)	$5·05 \times 10^{7}$	$4·08 \times 10^{7}$	$6·79 \times 10^{3}$	36·6	1·11	$9·20 \times 10^{-2}$	$1·49 \times 10^{-2}$	$3·77 \times 10^{-3}$	$1·33 \times 10^{-3}$
Isobutene (gas)+isobutane (gas) = 2,2,4-trimethylpentane (gas)	$1·74 \times 10^{5}$	$1·43 \times 10^{5}$	64·1	0·617	$2·75 \times 10^{-2}$	$3·14 \times 10^{-3}$	$6·65 \times 10^{-4}$	$2·10 \times 10^{-4}$	$8·45 \times 10^{-5}$
2-Methyl-2-butene (gas)+isobutane (gas) = 2,2,5-trimethylhexane (gas)	$5·13 \times 10^{3}$	$4·30 \times 10^{3}$	4·44	$7·45 \times 10^{-2}$	$4·86 \times 10^{-3}$	$7·35 \times 10^{-4}$	$2·00 \times 10^{-4}$	$7·59 \times 10^{-5}$	$3·48 \times 10^{-5}$

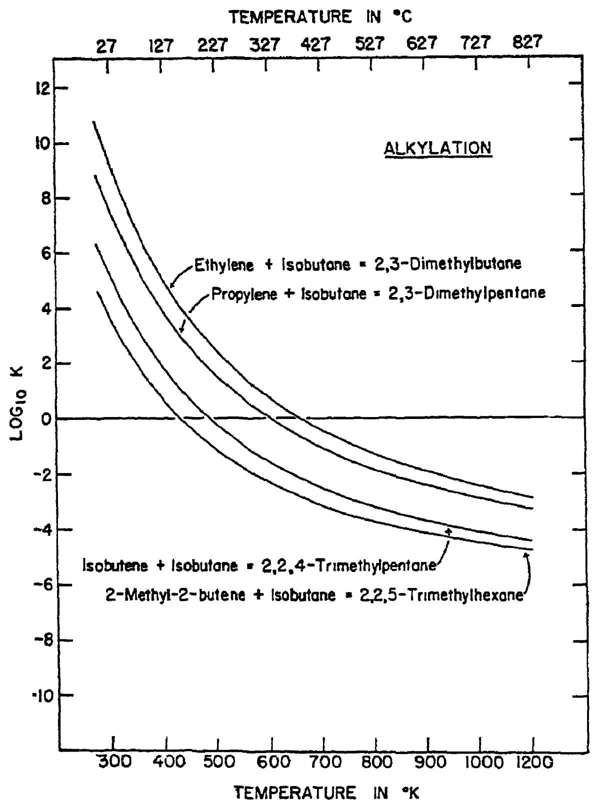


FIG. 22. Logarithm of the equilibrium constant for some reactions of alkylation.

The scale of ordinates gives the value of the logarithm (to the base 10) of the equilibrium constant for some reactions of alkylation (addition of an olefine to a paraffin to form a paraffin), in the gaseous state. The scale of abscissae gives the temperature in °K. and °C. The corresponding numerical values are given in Table VII.

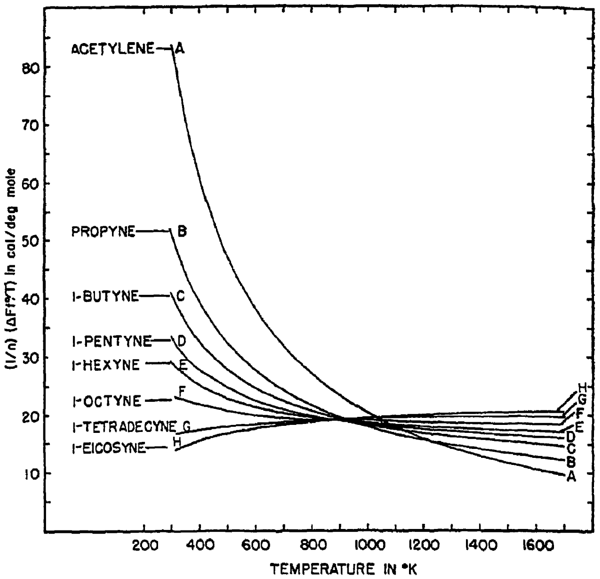


FIG. 23. Thermodynamic stability of the 1-alkyne hydrocarbons in the gaseous state as a function of temperature.

The scale of ordinates gives the value of $(1/n)$ $(\Delta Ff./T)$ in calories per degree mole, where n is the number of carbon atoms per molecule, T is the absolute temperature in °K., and ΔFf° is the standard-free energy of formation of the hydrocarbon from the elements, solid carbon (graphite), and gaseous hydrogen. The scale of abscissae gives the temperature in °K. Points below the zero-line indicate that the gaseous hydrocarbon in its standard state has a thermodynamic tendency to be formed from solid carbon (graphite) and gaseous hydrogen in their respective standard states.

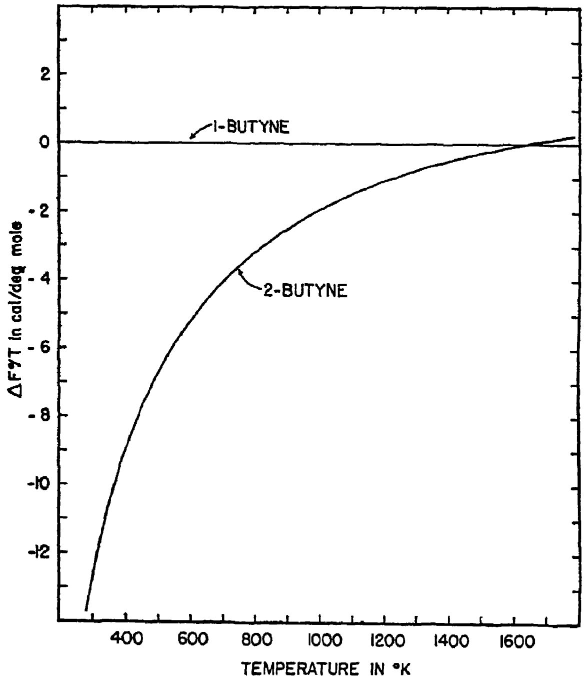


FIG. 24. Free energy of isomerization of the two butynes.

The scale of ordinates gives the value of $\Delta F./T$, in cal./deg. mole, for the isomerization of 1-butyne (gas) into 2-butyne (gas). The scale of abscissae gives the temperature in °K.

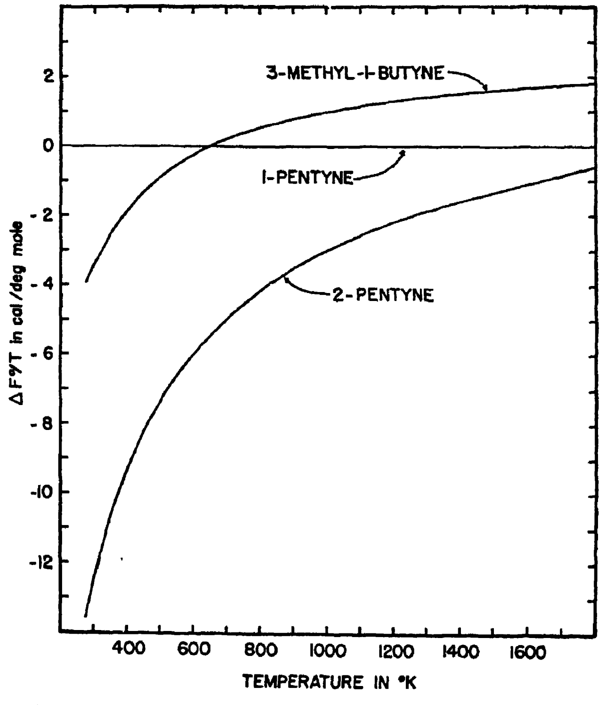


FIG. 25. Free energy of isomerization of the three pentynes.

The scale of ordinates gives the value of $\Delta F./T$, in cal./deg. mole, for the isomerization of 1-pentyne (gas) into the appropriate isomeric pentyne (gas). The scale of abscissae gives the temperature in °K.

sponding ones for the normal paraffins and the 1-alkene mono-olefines.

In Figs. 24 and 25 are plotted, as a function of the temperature, the values of Δ *F.*/*T* for the isomerization of the two butynes and the three pentynes, respectively, according to the reaction:

1-alkyne, normal (gas) = isomeric alkyne (gas). (25)

From these charts one may see at a glance, for any temperature in the given range, and within the assigned limits of uncertainty, which of the isomers is thermodynamically most stable (lowest value of Δ *F.*/*T*) and which is the least stable (highest value of Δ *F.*/*T*).

according to the following equations, for the paraffin, olefine, and acetylene series, respectively:

$$n\text{C(solid, graphite)} + (n+1)\text{H}_2\text{(gas)} = \text{C}_n\text{H}_{2n+2}\text{(gas, normal paraffin)} \quad (26)$$

$$n\text{C(solid, graphite)} + n\text{H}_2\text{(gas)} = \text{C}_n\text{H}_{2n}\text{(gas, 1-alkene)} \quad (27)$$

$$n\text{C(solid, graphite)} + (n-1)\text{H}_2\text{(gas)} = \text{C}_n\text{H}_{2n-2}\text{(gas, 1-alkyne)}. \quad (28)$$

The differences in the values of the ordinates of any given pair of curves in Figs. 28, 29, 30, and 31 give the value of the logarithm of the equilibrium constant for the appropriate reaction of hydrogenation or dehydrogenation.

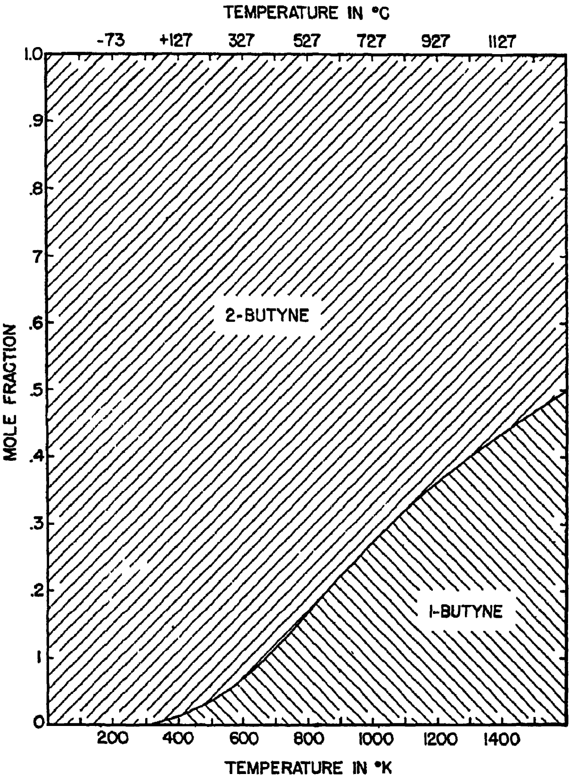


FIG. 26. Equilibrium concentrations of the two butynes.

The scale of ordinates measures the amount in mole fraction, and the scale of abscissae gives the temperature in °K. and °C. The vertical width of a band at a given temperature measures the mole fraction of the given isomer present when at equilibrium with all of its other isomers, in the gas phase.

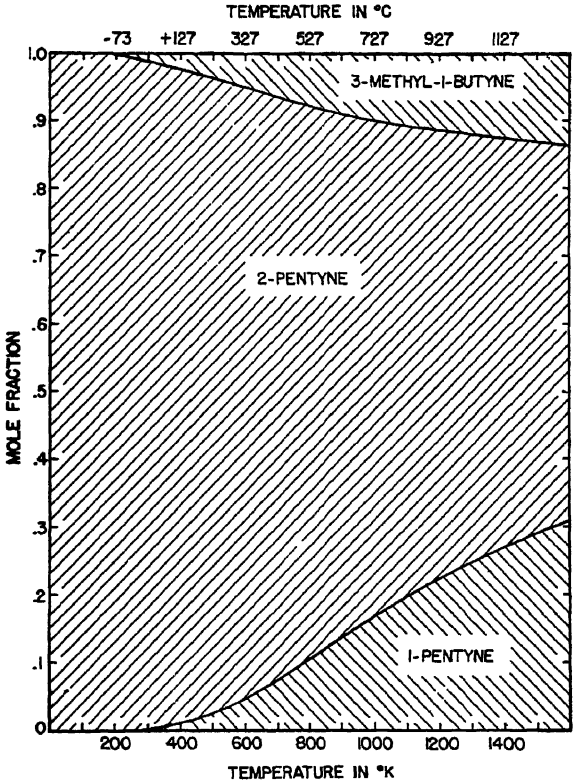


FIG. 27. Equilibrium concentrations of the three pentynes.

The scale of ordinates measures the amount in mole fraction, and the scale of abscissae gives the temperature in °K. and °C. The vertical width of a band at a given temperature measures the mole fraction of the given isomer present when at equilibrium with all of its other isomers, in the gas phase.

In Figs. 26 and 27 are plotted, as a function of temperature, for the butynes and pentynes, respectively, the amounts, in mole fraction, of each of the isomers present when at equilibrium with its other acetylene isomers in the gas phase. The vertical width of each band gives the mole fraction for that isomer at the selected temperature. The mole fractions of the several isomers are plotted additively, so that their sum is unity at all temperatures.

In Figs. 28, 29, 30, and 31 are plotted; as a function of temperature, for the C_2, C_3, C_4, and C_5 hydrocarbons, respectively, values of $\log_{10} Kf$, the logarithm (to the base 10) of the equilibrium constant, of the reaction of forming the given hydrocarbon in its standard gaseous state from the elements solid carbon (graphite) and gaseous hydrogen

Values of log *K* and *K* for the several reactions of dehydrogenation (and hydrogenation) are given in Table VIII.

The plots in Figs. 28, 29, 30, and 31 show, for molecules of the same number of carbon atoms, the ranges of temperature in which the normal paraffin, 1-alkene, and 1-alkyne hydrocarbons are relatively most stable (highest value of log *Kf*) in the presence of hydrogen, with each substance (including the hydrogen) in its thermodynamic standard state of unit fugacity of 1 atm. These ranges of temperature are given in Table IX in degrees Kelvin and centigrade, and are important in the analysis of any process involving hydrogenation or dehydrogenation of these molecules.

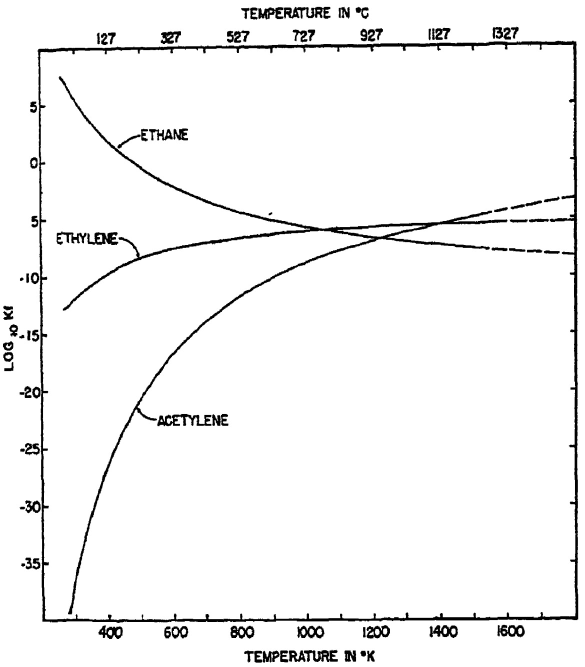


FIG. 28. Logarithm of the equilibrium constant of formation of ethane, ethylene, and acetylene.

The scale of ordinates gives the logarithm (to the base 10) of the equilibrium constant of formation of the hydrocarbons in the gaseous state from the elements solid carbon (graphite) and gaseous hydrogen, with each substance in its thermodynamic standard state of unit fugacity. The scale of abscissae gives the temperature in °K. and °C.

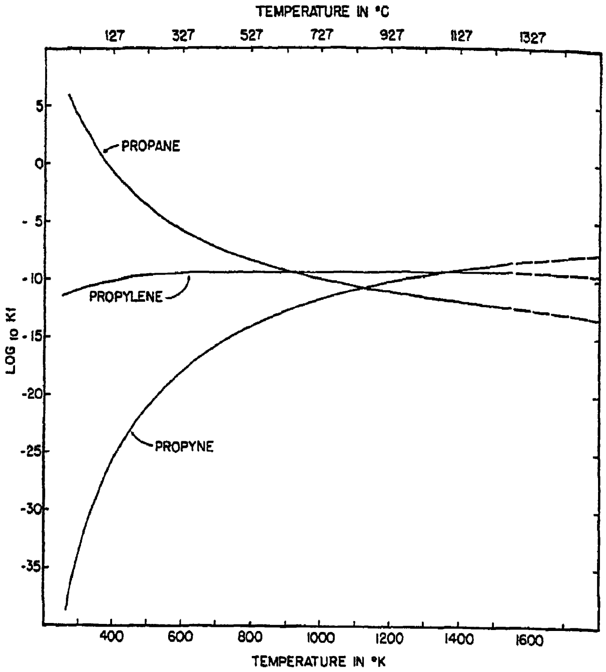


FIG. 29. Logarithm of the equilibrium constant of formation of propane, propylene, and propyne.

The scale of ordinates gives the logarithm (to the base 10) of the equilibrium constant of formation of the hydrocarbons from the elements solid carbon (graphite) and gaseous hydrogen, with each substance in its thermodynamic standard state of unit fugacity. The scale of abscissae gives the temperature in °K. and °C.

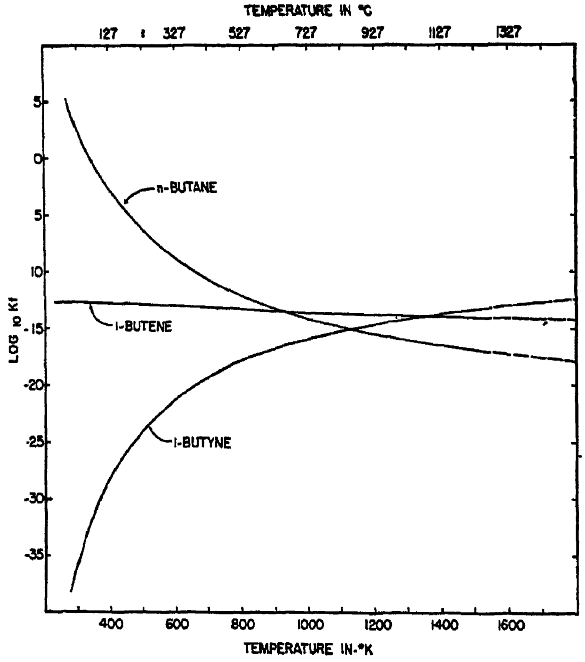


FIG. 30. Logarithm of the equilibrium constant of formation of *n*-butane, 1-butene, and 1-butyne.

The scale of ordinates gives the logarithm (to the base 10) of the equilibrium constant of formation of the hydrocarbons from the elements solid carbon (graphite) and gaseous hydrogen, with each substance in its thermodynamic standard state of unit fugacity. The scale of abscissae gives the temperature in °K. and °C.

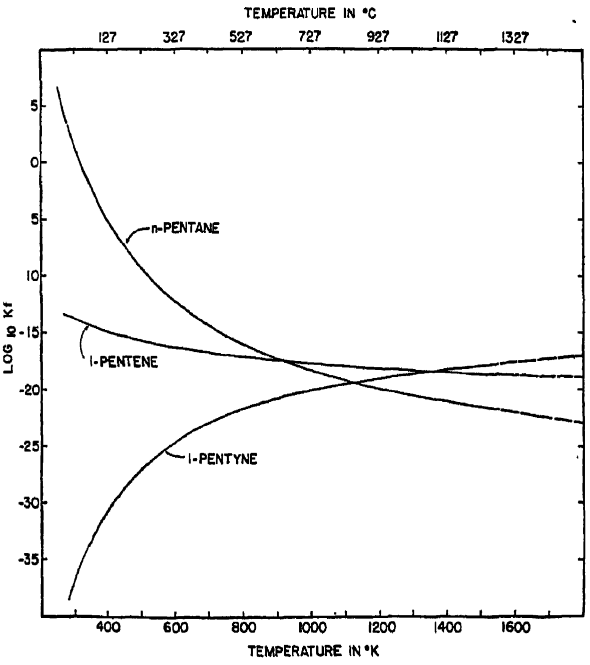


FIG. 31. Logarithm of the equilibrium constant of formation of *n*-pentane, 1-pentene, and 1-pentyne.

The scale of ordinates gives the logarithm (to the base 10) of the equilibrium constant of formation of the hydrocarbons from the elements solid carbon (graphite) and gaseous hydrogen, with each substance in its thermodynamic standard state of unit fugacity. The scale of abscissae gives the temperature in °K. and °C.

TABLE VIII

Logarithm of the Equilibrium Constant for the Dehydrogenation reactions involving n-Paraffins, 1-Alkenes, and 1-Alkynes, C_2 to C_5

Reaction	Temperature in °K.													
	298·16	300	400	500	600	700	800	900	1,000	1,100	1,200	1,300	1,400	1,500
	Logarithm of the equilibrium constant, $\log_{10} K$													
n-Paraffin (gas) = 1-alkene (gas)+H_2 (gas):														
C_2H_6 (gas) = C_2H_4 (gas)+H_2 (gas)	−17·6958	−17·5494	−11·5404	−7·9014	−5·4444	−3·6778	−2·3423	−1·2992	−0·4634	+0·2229	0·7937	1·2766	1·6897	2·0495
C_3H_8 (gas) = C_3H_6 (gas)+H_2 (gas)	−15·0835	−14·9822	−9·4954	−6·1897	−3·9594	−2·3572	−1·1504	−0·2095	+0·5422	1·1575	1·6702	2·1031	2·4749	2·8044
C_4H_{10} (gas) = C_4H_8 (gas)+H_2 (gas)	−15·3715	−15·2364	−9·7090	−6·3650	−4·1017	−2·4706	−1·2443	−0·2890	+0·4758	1·1039	1·6302	2·0772	2·4581	2·7908
C_5H_{12} (gas) = C_5H_{10} (gas)+H_2 (gas)	−15·2070	−15·0725	−9·5615	−6·2095	−3·9550	−2·3313	−1·1050	−0·1492	+0·6177	1·2431	1·7653	2·2042	2·5838	2·9200
n-Paraffin (gas) = 1-alkyne (gas)+2H_2 (gas):														
C_2H_6 (gas) = C_2H_2 (gas)+2H_2 (gas)	−42·4103	−42·0771	−28·4239	−20·1185	−14·5203	−10·4906	−7·4498	−5·0698	−3·1634	−1·6011	−0·2992	+0·8016	1·7437	2·5610
C_3H_8 (gas) = C_3H_4 (gas)+2H_2 (gas)	−38·0619	−37·8976	−25·1853	−17·4808	−12·2940	−8·5644	−5·7546	−3·5612	−1·8058	−0·3694	+0·8276	1·8385	2·7045	3·4620
C_4H_{10} (gas) = C_4H_6 (gas)+2H_2 (gas)	−38·3132	−38·0028	−25·2625	−17·5354	−12·3327	−8·5930	−5·7807	−3·5875	−1·8321	−0·3934	+0·8068	1·8220	2·6885	3·4415
C_5H_{12} (gas) = C_5H_8 (gas)+2H_2 (gas)	−38·2078	−37·8975	−25·1590	−17·4158	−12·2151	−8·4778	−5·6616	−3·4678	−1·7082	−0·2704	+0·9272	1·9376	2·8025	3·5608
1-Alkene (gas) = 1-alkyne (gas)+H_2 (gas):														
C_2H_4 (gas) = C_2H_2 (gas)+H_2 (gas)	−24·7145	−24·5277	−16·8835	−12·2171	−9·0759	−6·8128	−5·1075	−3·7706	−2·7000	−1·8240	−1·0929	−0·4750	+0·0540	0·5115
C_3H_6 (gas) = C_3H_4 (gas)+H_2 (gas)	−22·9784	−22·9154	−15·6899	−11·2911	−8·3346	−6·2072	−4·6042	−3·3517	−2·3480	−1·5269	−0·8426	−0·2646	+0·2296	0·6576
C_4H_8 (gas) = C_4H_6 (gas)+H_2 (gas)	−22·9417	−22·7664	−15·5535	−11·1704	−8·2310	−6·1224	−4·5364	−3·2985	−2·3079	−1·4973	−0·8234	−0·2552	+0·2304	0·6507
C_5H_{10} (gas) = C_5H_8 (gas)+H_2 (gas)	−23·0008	−22·8250	−15·5975	−11·2063	−8·2601	−6·1465	−4·5566	−3·3186	−2·3259	−1·5135	−0·8381	−0·2671	+0·2187	0·6408

TABLE IX

Ranges of Temperature in which, for Molecules of the Same Number of Carbon Atoms, the Normal Paraffin, 1-Alkene, and 1-Alkyne Hydrocarbons, C_2 to C_5, are relatively most stable in the presence of Hydrogen, with each Substance in its Thermodynamic Standard State

Number of C atoms	*n*-Paraffin		1-Alkene		1-Alkyne	
	Range of temperature*					
	°K.	°C.	°K.	°C.	°K.	°C.
	Below		Between		Above	
C_2	1,065	792	1,065–1,390	792–1,117	1,390	1,117
C_3	930	657	930–1,350	657–1,077	1,350	1,077
C_4	935	662	935–1,350	662–1,077	1,350	1,077
C_5	915	642	915–1,350	642–1,077	1,350	1,077

* Temperatures rounded to the nearest 5° K.

VI. Alkylbenzene Hydrocarbons

Taylor, Wagman, Williams, Pitzer, and Rossini [17] and Prosen, Johnson, and Rossini [14] have summarized the results on the thermodynamic properties of the alkylbenzenes.

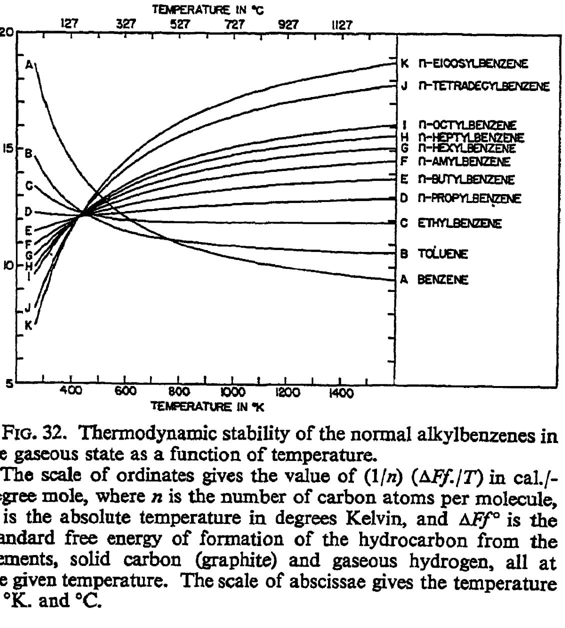


FIG. 32. Thermodynamic stability of the normal alkylbenzenes in the gaseous state as a function of temperature.

The scale of ordinates gives the value of $(1/n)$ $(\Delta Ff./T)$ in cal./degree mole, where n is the number of carbon atoms per molecule, T is the absolute temperature in degrees Kelvin, and $\Delta Ff°$ is the standard free energy of formation of the hydrocarbon from the elements, solid carbon (graphite) and gaseous hydrogen, all at the given temperature. The scale of abscissae gives the temperature in °K. and °C.

Fig. 32 shows the thermodynamic stability of the normal alkylbenzenes in the gaseous state as a function of the temperature, in the form of a plot of the standard-free energy of formation, per carbon atom, divided by the absolute temperature. This plot may be compared with the corresponding ones for the normal paraffins, the 1-alkene mono-olefines, and the 1-alkyne acetylenes.

In Figs. 33 and 34 are plotted, as a function of the temperature, the values of $\Delta F./T$ for the isomerization of the C_8H_{10} and C_9H_{12} alkylbenzenes, according to the reactions

$$\text{ethylbenzene (gas)} = \text{isomeric alkylbenzene (gas)} \tag{29}$$

$$n\text{-propylbenzene (gas)} = \text{isomeric alkylbenzene (gas).} \tag{30}$$

From these plots one may see at a glance, for any temperature in the given range, and within the assigned limits of uncertainty, which of the isomers is thermodynamically most stable (lowest value of $\Delta F./T$) and which is the least stable (highest value of $\Delta F./T$).

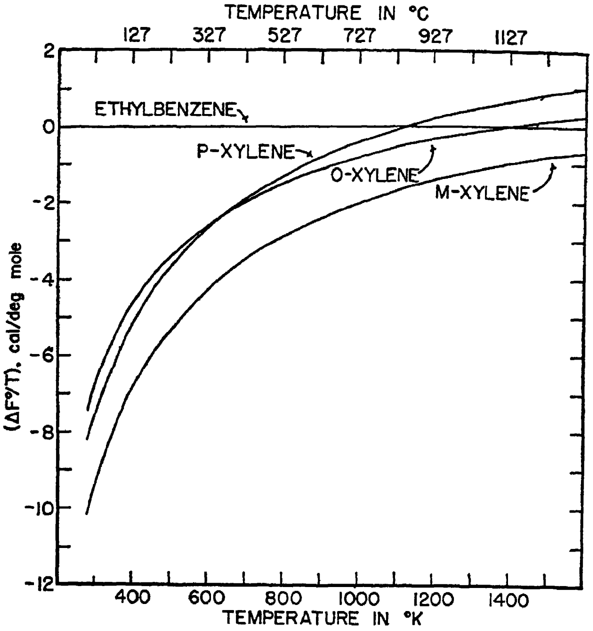


FIG. 33. Free energy of isomerization of the C_8H_{10} alkylbenzenes.

The scale of ordinates gives the value of $\Delta F./T$, in calories per degree mole, for the isomerization of ethylbenzene into the other isomers, in the gaseous state, as indicated. The scale of abscissae gives the temperature in °K. and °C.

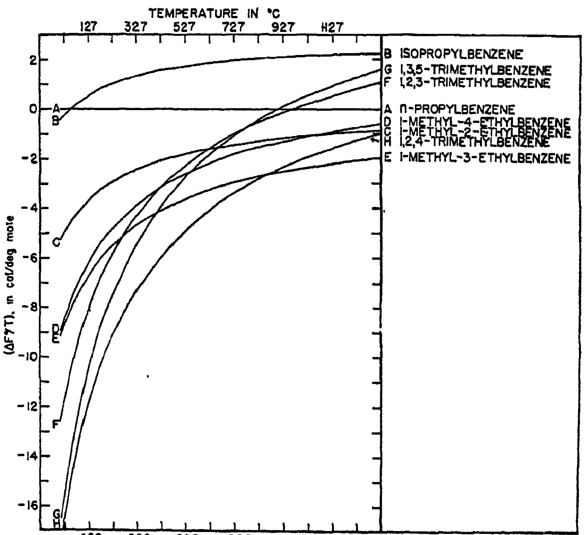


FIG. 34. Free energy of isomerization of the C_9H_{12} alkylbenzenes.

The scale of ordinates gives the value of $\Delta F./T$, in calories per degree mole, for the isomerization of n-propylbenzene into the other isomers, in the gaseous state, as indicated. The scale of abscissae gives the temperature in °K. and °C.

In Figs. 35 and 36 are plotted, as a function of temperature, for the C_8H_{10} and the C_9H_{12} alkylbenzenes, respectively, the amounts, in mole fraction, of each of the isomers present at equilibrium with its other isomers in the gas phase. The vertical width of each band gives the mole fraction for that isomer at the selected temperature. The mole fractions of the several isomers are plotted additively, so that their sum is unity at all temperatures.

Table X presents values of the equilibrium constant, and of its logarithm, for some reactions of alkylation (addition

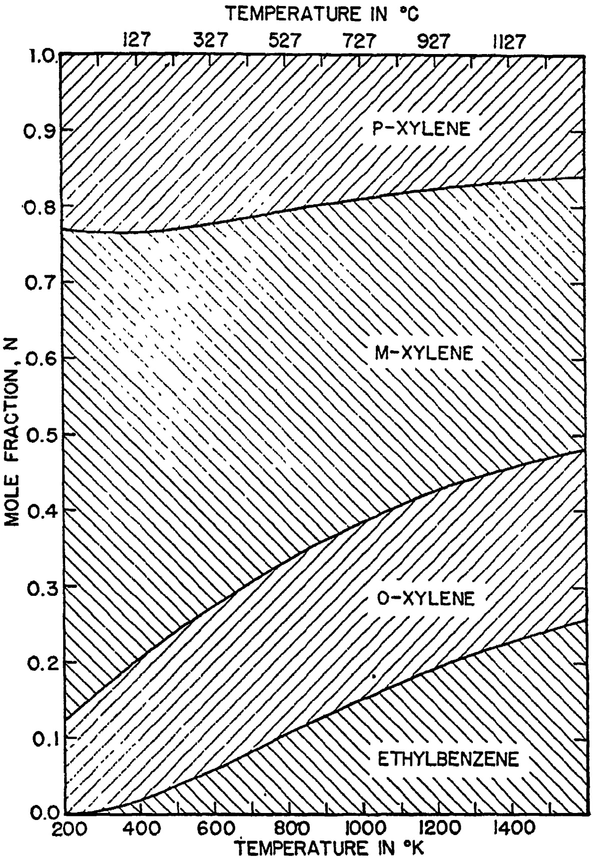


FIG. 35. Equilibrium concentrations of the C_8H_{10} alkylbenzenes.

The scale of ordinates measures the amount in mole fraction, and the scale of abscissae gives the temperature in degrees Kelvin and degrees centigrade. The vertical width of a band at a given temperature measures the mole fraction of the given isomer present when at equilibrium with all of its other isomers, in the gas phase.

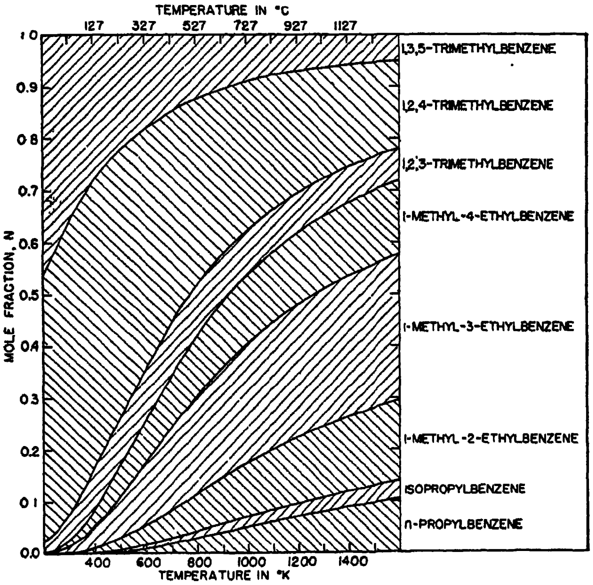


FIG. 36. Equilibrium concentrations of the C_9H_{12} alkylbenzenes.

The scale of ordinates measures the amount in mole fraction, and the scale of abscissae gives the temperature in degrees Kelvin and degrees centigrade. The vertical width of a band at a given temperature measures the mole fraction of the given isomer present when at equilibrium with all of its other isomers, in the gas phase.

of an olefine to benzene to form an alkylbenzene), cyclization (conversion of normal paraffin to alkylbenzene plus hydrogen), and trimerization (of acetylene to benzene and of methylacetylene to 1,3,5-trimethylbenzene), for the following reactions:

Alkylation

benzene (gas) + ethylene (gas)
= ethylbenzene (gas) (31)
benzene (gas) + propylene (gas)
= *n*-propylbenzene (gas) (32)
benzene (gas) + propylene (gas)
= isopropylbenzene (gas) (33)
benzene (gas) + C_nH_{2n}(1-alkene, normal, gas)
= *n*-alkylbenzene (gas); $n > 3$. (34)

Cyclization

n-hexane (gas)
= benzene (gas) + hydrogen (gas) (35)
n-heptane (gas)
= toluene (gas) + hydrogen (gas) (36)
n-octane (gas)
= ethylbenzene (gas) + hydrogen (gas) (37)
n-nonane (gas)
= *n*-propylbenzene (gas) + hydrogen (gas) (38)
n-paraffin (gas)
= *n*-alkylbenzene (gas)
+ hydrogen (gas); above nonane. (39)

Trimerization

acetylene (gas) = benzene (gas) (40)
methylacetylene (gas) = 1,3,5-trimethylbenzene (gas). (41)

In Figs. 37, 38, and 39 are plotted, as a function of temperature, values of the logarithm of the equilibrium constant for the above reactions of alkylation, cyclization, and trimerization, respectively.

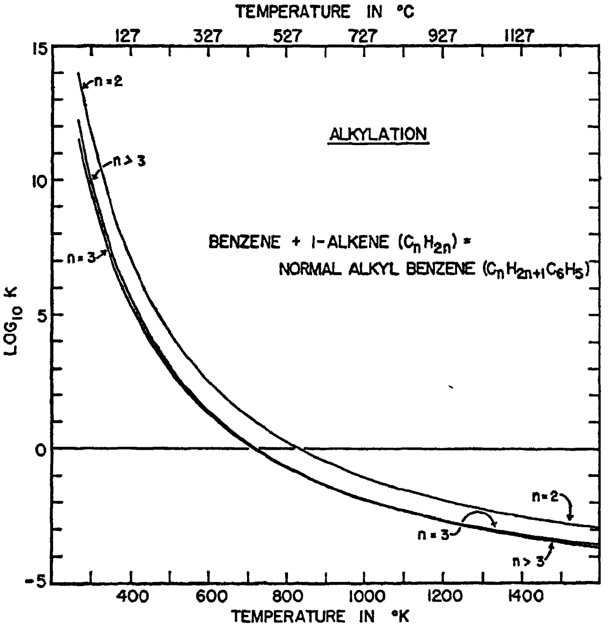


FIG. 37. Logarithm of the equilibrium constant for some reactions of alkylation.

The scale of ordinates gives the value of the logarithm (to the base 10) of the equilibrium constant for some reactions of alkylation (addition of an olefine to benzene to form an alkyl benzene), in the gaseous state. The scale of abscissae gives the temperature in degrees Kelvin and degrees centigrade. The corresponding numerical values are given in table X.

TABLE X

Values of Equilibrium Constants for Reactions of Alkylation, Cyclization, and Trimerization, to 1,500° K.

Reaction	*Temperature in °K.*													
	298·16	*300*	*400*	*500*	*600*	*700*	*800*	*900*	*1,000*	*1,100*	*1,200*	*1,300*	*1,400*	*1,500*
	Logarithm of the equilibrium constant, $\log_{10} K$.													
Alkylation														
C_6H_6 (benzene, gas)+C_2H_4 (ethylene, gas) = C_8H_{10} (ethylbenzene, gas)	11·7738	11·6605	7·0710	4·3417	2·5261	1·2382	0·2806	−0·4584	−1·0455	−1·5223	−1·9155	−2·2445	−2·5240	−2·7665
C_6H_6 (benzene, gas)+C_3H_6 (propylene, gas) = C_9H_{12} (*n*-propylbenzene, gas)	9·634	9·531	5·380	2·928	1·295	0·145	−0·707	−1·365	−1·881	−2·302	−2·654	−2·947	−3·196	−3·403
C_6H_6 (benzene, gas)+C_3H_6 (propylene, gas) = C_9H_{12} (isopropylbenzene, gas)	9·686	9·579	5·257	2·698	1·000	−0·200	−1·088	−1·771	−2·314	−2·754	−3·117	−3·417	−3·672	−3·889
C_6H_6 (benzene, gas)+C_nH_{2n} (1-alkene, gas) = $C_nH_{2n+1}C_6H_5$ (*n*-alkylbenzene, gas) $n>3$	9·960	9·851	5·593	3·068	1·390	0·202	−0·680	−1·357	−1·895	−2·333	−2·698	−3·003	−3·262	−3·483
Cyclization														
C_6H_{14} (*n*-hexane, gas) = C_6H_6 (benzene, gas)+$4H_2$ (gas)	−22·677	−22·406	−11·418	−4·712	−0·176	+3·097	5·566	7·494	9·041	10·308	11·365	12·258	13·021	13·686
C_7H_{16} (*n*-heptane, gas) = C_7H_8 (toluene, gas)+$4H_2$ (gas)	−19·892	−19·636	−9·184	−2·806	+1·502	4·613	6·956	8·785	10·251	11·448	12·448	13·294	14·018	14·654
C_8H_{18} (*n*-octane, gas) = C_8H_{10} (ethylbenzene, gas)+$4H_2$ (gas)	−19·840	−19·587	−9·144	−2·724	+1·597	4·718	7·067	8·905	10·378	11·584	12·588	13·441	14·172	14·817
C_9H_{20} (*n*-nonane, gas) = C_9H_{12} (*n*-propylbenzene, gas)+$4H_2$ (gas)	−19·516	−19·263	−8·849	−2·487	+1·813	4·918	7·259	9·085	10·553	11·751	12·746	13·591	14·318	14·968
C_nH_{2n+2} (*n*-paraffin, gas) = C_nH_{2n-6} (*n*-alkylbenzene, gas)+$4H_2$ (gas); $n>9$	−19·341	−19·092	−8·721	−2·393	+1·890	4·981	7·310	9·133	10·593	11·784	12·776	13·618	14·344	14·992
Trimerization														
$3C_2H_2$ (acetylene, gas) = C_6H_6 (benzene, gas)	87·2327	86·5922	60·4947	44·7349	34·1816	26·6256	20·9589	16·5390	13·0126	10·1321	7·7369	5·7151	3·9862	2·4941
$3C_3H_4$ (methylacetylene, gas) = C_9H_{12} (1,3,5-trimethylbenzene, gas)	81·191	80·916	55·895	40·845	30·789	23·598	18·205	14·012	10·664	7·930	5·657	3·740	2·102	0·688
	Equilibrium constant K													
Alkylation														
C_6H_6 (benzene, gas)+C_2H_4 (ethylene, gas) = C_8H_{10} (ethylbenzene, gas)	$5·940\times10^{11}$	$4·576\times10^{11}$	$1·178\times10^{7}$	$2·196\times10^{4}$	$3·358\times10^{2}$	17·31	1·908	0·3480	$9·005\times10^{-2}$	$3·004\times10^{-2}$	$1·215\times10^{-2}$	$5·695\times10^{-3}$	$2·992\times10^{-3}$	$1·712\times10^{-3}$
C_6H_6 (benzene, gas)+C_3H_6 (propylene, gas) = C_9H_{12} (*n*-propylbenzene, gas)	$4·30\times10^{9}$	$3·40\times10^{9}$	$2·40\times10^{5}$	$8·47\times10^{2}$	19·72	1·397	$1·96\times10^{-1}$	$4·32\times10^{-2}$	$1·31\times10^{-2}$	$4·99\times10^{-3}$	$2·22\times10^{-3}$	$1·13\times10^{-3}$	$6·37\times10^{-4}$	$3·95\times10^{-4}$
C_6H_6 (benzene, gas)+C_3H_6 (propylene, gas) = C_9H_{12} (isopropylbenzene, gas)	$4·85\times10^{9}$	$3·79\times10^{9}$	$1·81\times10^{5}$	$4·99\times10^{2}$	10·00	0·631	$8·16\times10^{-2}$	$1·69\times10^{-2}$	$4·85\times10^{-3}$	$1·76\times10^{-3}$	$7·64\times10^{-4}$	$3·83\times10^{-4}$	$2·13\times10^{-4}$	$1·29\times10^{-4}$
C_6H_6 (benzene, gas)+C_nH_{2n} (1-alkene, gas) = $C_nH_{2n+1}C_6H_5$ (*n*-alkylbenzene, gas); $n>3$	$9·12\times10^{9}$	$7·10\times10^{9}$	$3·92\times10^{5}$	$1·17\times10^{3}$	24·55	1·592	0·209	$4·40\times10^{-2}$	$1·27\times10^{-2}$	$4·64\times10^{-3}$	$2·00\times10^{-3}$	$9·93\times10^{-4}$	$5·47\times10^{-4}$	$3·29\times10^{-4}$
Cyclization														
C_6H_{14} (*n*-hexane, gas) = C_6H_6 (benzene, gas)+$4H_2$ (gas)	$2·10\times10^{-23}$	$3·93\times10^{-23}$	$3·82\times10^{-12}$	$1·94\times10^{-5}$	0·667	$1·25\times10^{3}$	$3·68\times10^{5}$	$3·12\times10^{7}$	$1·10\times10^{9}$	$2·03\times10^{10}$	$2·32\times10^{11}$	$1·81\times10^{12}$	$1·05\times10^{13}$	$4·85\times10^{13}$
C_7H_{16} (*n*-heptane, gas) = C_7H_8 (toluene, gas)+$4H_2$ (gas)	$1·28\times10^{-20}$	$2·31\times10^{-20}$	$6·54\times10^{-10}$	$1·56\times10^{-3}$	31·77	$4·10\times10^{4}$	$9·03\times10^{6}$	$6·10\times10^{8}$	$1·78\times10^{10}$	$2·80\times10^{11}$	$2·80\times10^{12}$	$1·97\times10^{13}$	$1·04\times10^{14}$	$4·51\times10^{14}$
C_8H_{18} (*n*-octane, gas) = C_8H_{10} (ethylbenzene, gas)+$4H_2$ (gas)	$1·45\times10^{-20}$	$2·59\times10^{-20}$	$7·18\times10^{-10}$	$1·89\times10^{-3}$	39·54	$5·22\times10^{4}$	$1·17\times10^{7}$	$8·03\times10^{8}$	$2·39\times10^{10}$	$3·84\times10^{11}$	$3·87\times10^{12}$	$2·76\times10^{13}$	$1·49\times10^{14}$	$6·56\times10^{14}$
C_9H_{20} (*n*-nonane, gas) = C_9H_{12} (*n*-propylbenzene, gas)+$4H_2$ (gas)	$3·05\times10^{-20}$	$5·46\times10^{-20}$	$1·42\times10^{-9}$	$3·26\times10^{-3}$	65·02	$8·28\times10^{4}$	$1·81\times10^{7}$	$1·22\times10^{9}$	$3·57\times10^{10}$	$5·64\times10^{11}$	$5·57\times10^{12}$	$3·90\times10^{13}$	$2·08\times10^{14}$	$9·29\times10^{14}$
C_nH_{2n+2} (*n*-paraffin, gas) = C_nH_{2n-6} (*n*-alkylbenzene, gas)+$4H_2$ (gas); $n>9$	$4·56\times10^{-20}$	$8·09\times10^{-20}$	$1·90\times10^{-9}$	$4·04\times10^{-3}$	77·70	$9·57\times10^{4}$	$2·04\times10^{7}$	$1·36\times10^{9}$	$3·92\times10^{10}$	$6·08\times10^{11}$	$5·97\times10^{12}$	$4·15\times10^{13}$	$2·21\times10^{14}$	$9·82\times10^{14}$
Trimerization														
$3C_2H_2$ (acetylene, gas) = C_6H_6 (benzene, gas)	$1·709\times10^{87}$	$3·910\times10^{86}$	$3·124\times10^{60}$	$5·431\times10^{44}$	$1·519\times10^{34}$	$4·223\times10^{26}$	$9·097\times10^{20}$	$3·460\times10^{16}$	$1·030\times10^{13}$	$1·356\times10^{10}$	$5·456\times10^{7}$	$5·190\times10^{5}$	$9·687\times10^{3}$	$3·120\times10^{2}$
$3C_3H_4$ (methylacetylene, gas) = C_9H_{12} (1,3,5-trimethylbenzene, gas)	$1·55\times10^{81}$	$8·24\times10^{80}$	$7·85\times10^{55}$	$7·00\times10^{40}$	$6·15\times10^{30}$	$3·96\times10^{23}$	$1·60\times10^{18}$	$1·03\times10^{14}$	$4·61\times10^{10}$	$8·51\times10^{7}$	$4·54\times10^{5}$	$5·50\times10^{3}$	$1·26\times10^{2}$	4·88

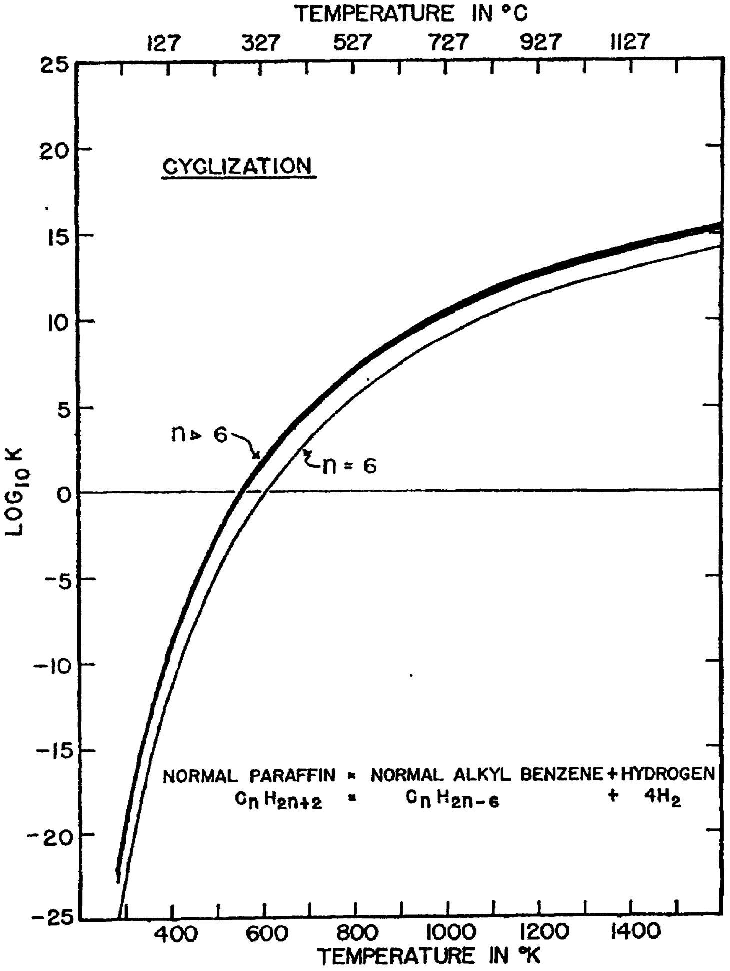


FIG. 38. Logarithm of the equilibrium constant for some reactions of cyclization.

The scale of ordinates gives the value of the logarithm (to the base 10) of the equilibrium constant for the reaction of cyclization of a normal paraffin to form a normal alkyl benzene, in the gaseous state. The scale of abscissae gives the temperature in degrees Kelvin and degrees centigrade. The values calculated for *n*-heptane and higher paraffins fall within the width of the heavy line indicated. The corresponding numerical values are given in table X.

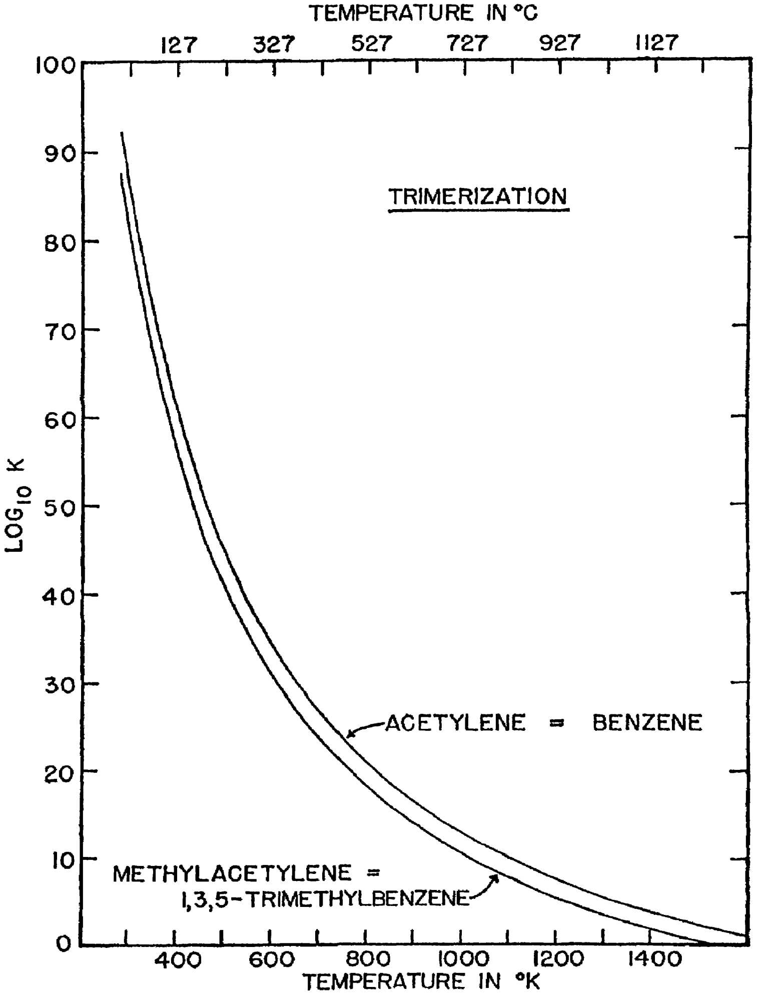


FIG. 39. Logarithm of the equilibrium constant for some reactions of trimerization.

The scale of ordinates gives the value of the logarithm (to the base 10) of the equilibrium constant for some reactions of trimerization of alkynes to alkylbenzenes, in the gaseous state. The scale of abscissae gives the temperature in degrees Kelvin and degrees centigrade. The corresponding numerical values are given in table X.

VII. Alkylcyclopentane Hydrocarbons

Kilpatrick, Beckett, Werner, Pitzer, and Rossini [31] and Prosen, Johnson, and Rossini [16] have summarized the results on the thermodynamic properties of the alkylcyclopentane hydrocarbons.

Fig. 40 shows the thermodynamic stability of the normal alkylcyclopentanes in the gaseous state as a function of the temperature, in the form of a plot of the standard free energy of formation, per carbon atom, divided by the absolute temperature. This plot may be compared with the corresponding ones for the normal paraffins, the 1-alkene mono-olefines, the 1-alkyne acetylenes, and the normal alkylbenzenes.

Fig. 41 gives a plot of the logarithm of the equilibrium constant, as a function of the temperature, for the following reactions of cyclization of normal paraffins to normal alkylcyclopentanes:

n-pentane (gas)
= cyclopentane (gas)+hydrogen (gas) (42)
n-hexane (gas)
= methylcyclopentane (gas)+hydrogen (gas) (43)
n-heptane (gas)
= ethylcyclopentane (gas)+hydrogen (gas) (44)
n-paraffin (gas)
= *n*-alkylcyclopentane (gas)+hydrogen (gas);
for *n*-octane and higher. (45)

Fig. 42 gives a plot of the logarithm of the equilibrium constant, as a function of the temperature, for the following reactions of hydrogenation of normal alkylbenzenes to normal alkylcyclopentanes:

benzene (gas)+hydrogen (gas)
= methylcyclopentane (gas) (46)
toluene (gas)+hydrogen (gas)
= ethylcyclopentane (gas) (47)
ethylbenzene (gas)+hydrogen (gas)
= *n*-propylcyclopentane (gas) (48)
n-propylbenzene (gas)+hydrogen (gas)
= *n*-butylcyclopentane (gas) (49)
n-alkylbenzene (gas)+hydrogen (gas)
= *n*-alkylcyclopentane (gas); for
n-butylbenzene and higher. (50)

Fig. 43 gives a plot of the logarithm of the equilibrium constant, as a function of the temperature, for the following reactions of cyclization of 1-alkene mono-olefines to normal alkylcyclopentanes:

1-pentene (gas) = cyclopentane (gas) (51)
1-hexene (gas) = methylcyclopentane (gas) (52)
1-heptene (gas) = ethylcyclopentane (gas) (53)
1-alkene (gas) = *n*-alkylcyclopentane (gas);
for 1-octene and higher. (54)

VIII. Alkylcyclohexane Hydrocarbons

Kilpatrick, Beckett, Werner, Pitzer, and Rossini [31] and Prosen, Johnson, and Rossini [16, 27] have summarized the results on the thermodynamic properties of the alkylcyclohexane hydrocarbons.

Fig. 44 shows the thermodynamic stability of the normal alkylcyclohexanes in the gaseous state as a function of the temperature, in the form of a plot of the standard free energy of formation, per carbon atom, divided by the

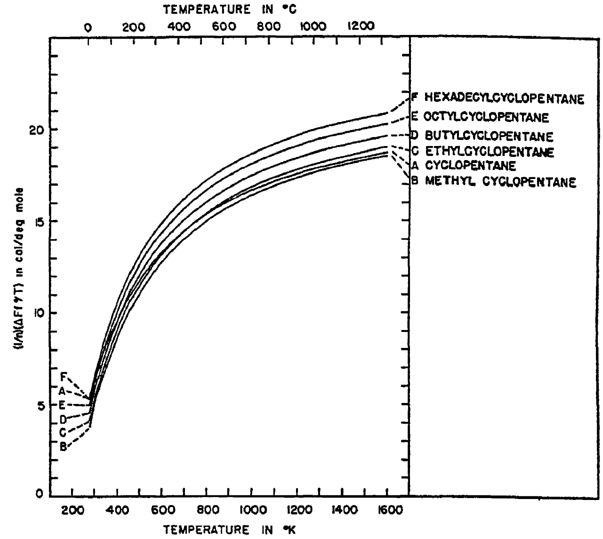


Fig. 40. Thermodynamic stability of the normal alkylcyclopentanes in the gaseous state as a function of temperature.

The scale of ordinates gives the value of $(1/n)$ $(\Delta Ff./T)$ in calories per degree mole, where n is the number of carbon atoms per molecule, T is the absolute temperature in degrees Kelvin, and $\Delta F_f{}^\circ$ is the standard free energy of formation of the hydrocarbon from the elements, solid carbon (graphite) and gaseous hydrogen. The scale of abscissae gives the temperature in °K. and °C. Points below the zero line indicate that the gaseous hydrocarbon in its standard state has a thermodynamic tendency to be formed from soild carbon (graphite) and gaseous hydrogen in their respective standard states.

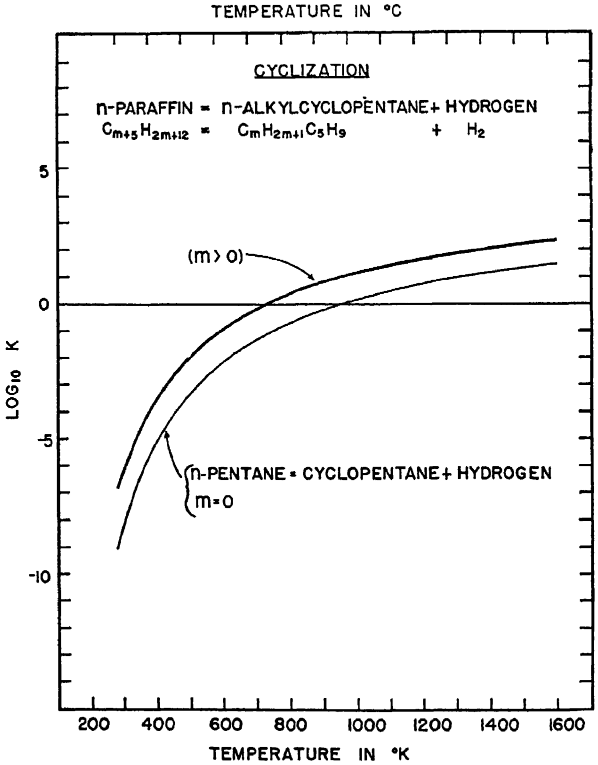


Fig. 41. Logarithm of the equilibrium constant for the reaction of cyclization of normal paraffins to normal alkylcyclopentanes.

The scale of ordinates gives the value of the logarithm (to the base 10) of the equilibrium constant for the reaction of cyclization of a given normal paraffin to the corresponding normal alkylcyclopentane, in the gaseous state. The scale of abscissae gives the temperature in °K. and °C. The values for the cyclization to methylcyclopentane, ethylcyclopentane, and the higher normal alkylcyclopentanes all fall within the width of the heavy line indicated.

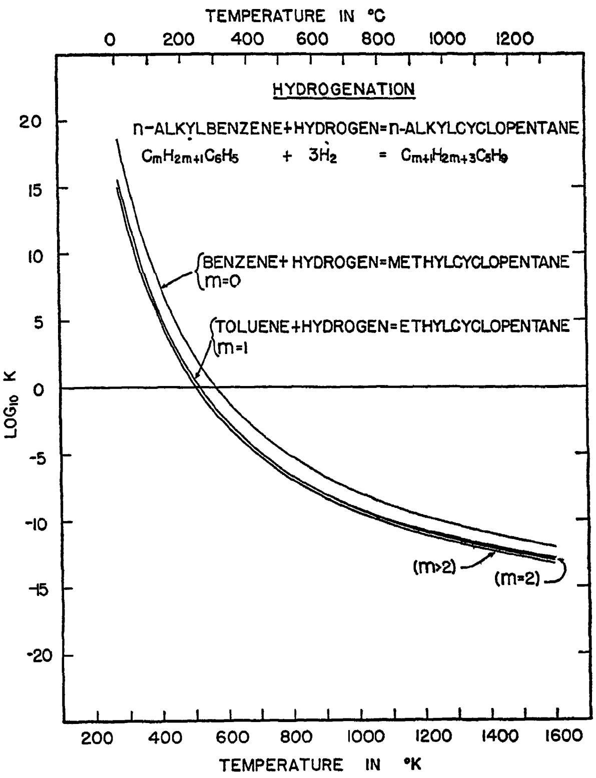


FIG. 42. Logarithm of the equilibrium constant for the reaction of hydrogenation of normal alkylbenzenes to normal alkylcyclopentanes.

The scale of ordinates gives the value of the logarithm (to the base 10) of the equilibrium constant for the reaction of hydrogenation of a given normal alkylbenzene to the corresponding normal alkylcyclopentane, in the gaseous state. The scale of abscissae gives the temperature in °K. and °C.

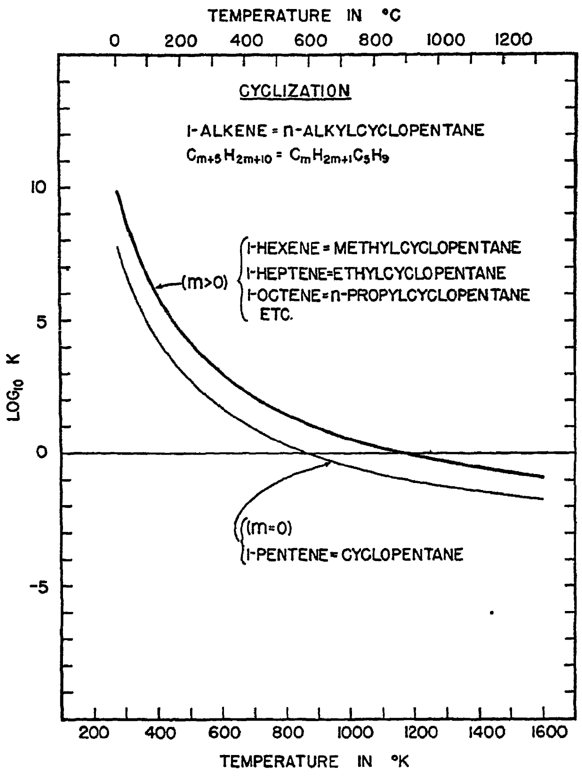


FIG. 43. Logarithm of the equilibrium constant for the reaction of cyclization of 1-alkene mono-olefines to normal alkylcyclopentanes.

The scale of ordinates gives the value of the logarithm (to the base 10) of the equilibrium constant for the reaction of cyclization of a given 1-alkene mono-olefine to the corresponding normal alkylcyclopentane, in the gaseous state. The scale of abscissae gives the temperature in °K. and °C. The values for the formation of methylcyclopentane, ethylcyclopentane, and higher normal alkylcyclopentanes all fall within the width of the heavy line.

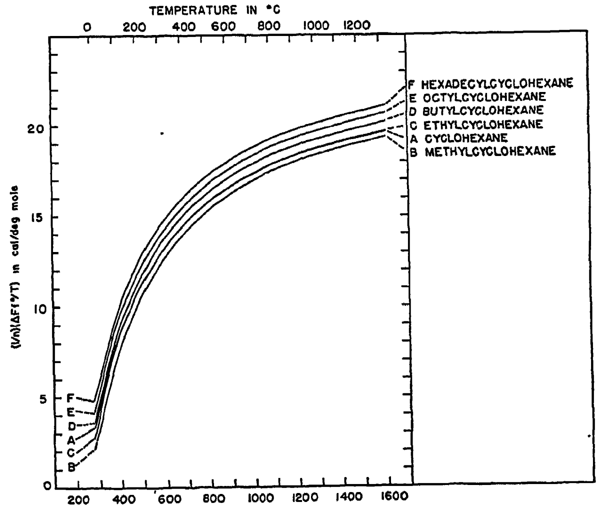


FIG. 44. Thermodynamic stability of the normal alkylcyclohexanes in the gaseous state as a function of temperature.

The scale of ordinates gives the value of $(1/n)$ $(\Delta F./T)$ in calories per degree mole, where n is the number of carbon atoms per molecule, T is the absolute temperature in degrees Kelvin, and $\Delta F°$ is the standard free energy of formation of the hydrocarbon from the elements, solid carbon (graphite) and gaseous hydrogen. The scale of abscissae gives the temperature in °K. and °C. Points below the zero line indicate that the gaseous hydrocarbon in its standard state has a thermodynamic tendency to be formed from solid carbon (graphite) and gaseous hydrogen in their respective standard states.

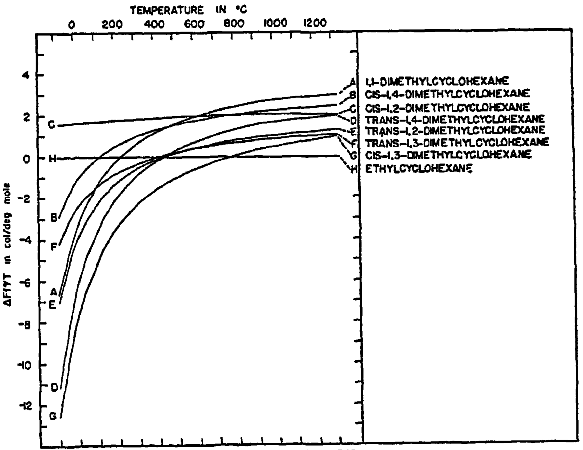


FIG. 45. Free energy of isomerization of the eight C_8H_{16} alkylcyclohexanes.

The scale of ordinates gives the value of $\Delta F./T$, in cal./deg. mole, for the isomerization of ethylcyclohexane into the other isomers, in the gaseous state, as indicated. The scale of abscissae gives the temperature in °K. and °C.

absolute temperature. This plot may be compared with the corresponding ones for the normal paraffins, the 1-alkene mono-olefines, the 1-alkyne acetylenes, the normal alkyl-benzenes, and the normal alkylcyclopentanes.

In Fig. 45 is plotted, as a function of the temperature, the values of $\Delta F/T$ for the isomerization of the C_8H_{16} alkylcyclohexanes, according to the reaction

ethylcyclohexane (gas) = dimethylcyclohexane (gas). (55)

From this plot one may see at a glance, for any temperature in the given range, and within the assigned limits of uncertainty, which of the isomers is thermodynamically most stable (lowest value of $\Delta F/T$) and which is the least stable (highest value of $\Delta F/T$).

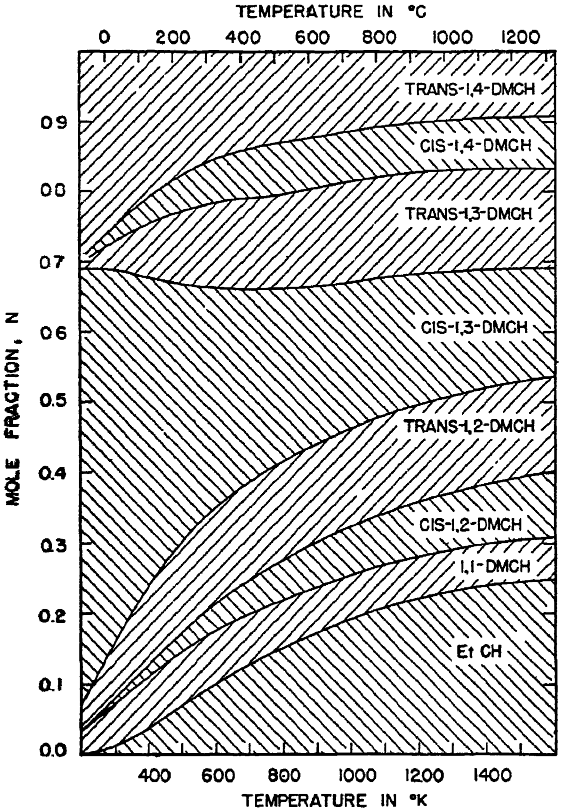


FIG. 46. Equilibrium concentrations of the eight C_8H_{16} alkylcyclohexanes.

The scale of ordinates measures the amount in mole fraction, and the scale of abscissae gives the temperature in degrees Kelvin and degrees centigrade. The vertical width of a band at a given temperature measures the mole fraction of the given isomer present when at equilibrium with all of its other isomers, in the gas phase.

In Fig. 46 is plotted, as a function of the temperature, for the C_8H_{16} alkylcyclohexanes, the amounts, in mole fraction, of each of the isomers present at equilibrium with its other isomers in the gas phase. The vertical width of each band gives the mole fraction for that isomer at the selected temperature. The mole fractions of the several isomers are plotted additively, so that their sum is unity at all temperatures.

Fig. 47 gives a plot of the logarithm of the equilibrium constant, as a function of the temperature, for the following reactions of cyclization of normal paraffins to normal alkylcyclohexanes:

n-hexane (gas)
= cyclohexane (gas) + hydrogen (gas) (56)
n-heptane (gas)
= methylcyclohexane (gas) + hydrogen (gas) (57)
n-octane (gas)
= ethylcyclohexane (gas) + hydrogen (gas) (58)
n-paraffin (gas)
= *n*-alkylcyclohexane (gas) + hydrogen (gas);
for *n*-nonane and higher. (59)

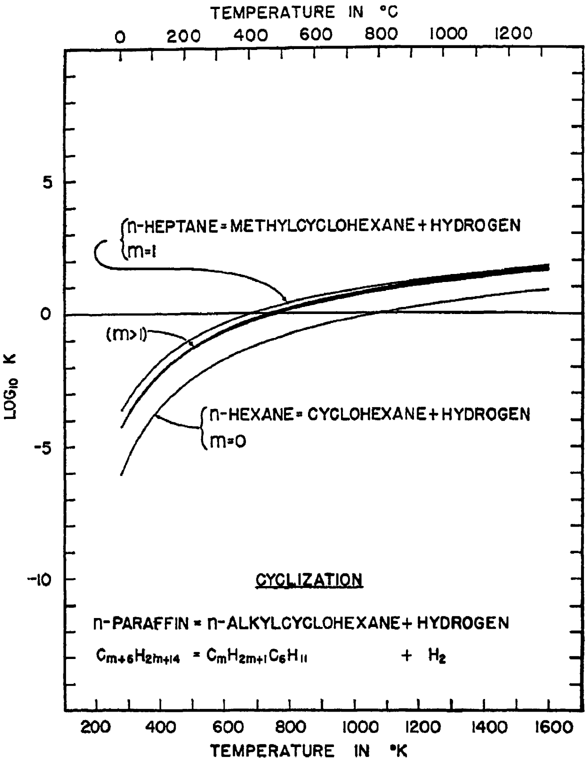


FIG. 47. Logarithm of the equilibrium constant for the reaction of cyclization of normal paraffins to normal alkylcyclohexanes.

The scale of ordinates gives the value of the logarithm (to the base 10) of the equilibrium constant for the reaction of cyclization of a given normal paraffin to the corresponding normal alkylcyclohexane, in the gaseous state. The scale of abscissae gives the temperature in °K. and °C. The values calculated for ethylcyclohexane, *n*-propylcyclohexane, and the higher normal alkylcyclohexanes all fall within the width of the heavy line.

Fig. 48 gives a plot of the logarithm of the equilibrium constant, as a function of the temperature, for the following reactions of conversion of normal alkylcyclohexanes to normal alkylcyclopentanes:

cyclohexane (gas)
= methylcyclopentane (gas) (60)
methylcyclohexane (gas)
= ethylcyclopentane (gas) (61)
ethylcyclohexane (gas)
= *n*-propylcyclopentane (gas) (62)
n-propylcyclohexane (gas)
= *n*-butylcyclopentane (gas) (63)
n-alkylcyclohexane (gas)
= *n*-alkylcyclopentane (gas);
for *n*-butylcyclohexane and higher. (64)

Fig. 49 gives a plot of the logarithm of the equilibrium constant, as a function of the temperature, for the following reactions of hydrogenation of normal alkylbenzenes to normal alkylcyclohexanes:

benzene (gas)+hydrogen (gas)
= cyclohexane (gas) (65)
toluene (gas)+hydrogen (gas)
= methylcyclohexane (gas) (66)
ethylbenzene (gas)+hydrogen (gas)
= ethylcyclohexane (gas) (67)
n-propylbenzene (gas)+hydrogen (gas)
= *n*-propylcyclohexane (gas) (68)
n-alkylbenzene (gas)+hydrogen (gas)
= *n*-alkylcyclohexane (gas);
for *n*-butylbenzene and higher. (69)

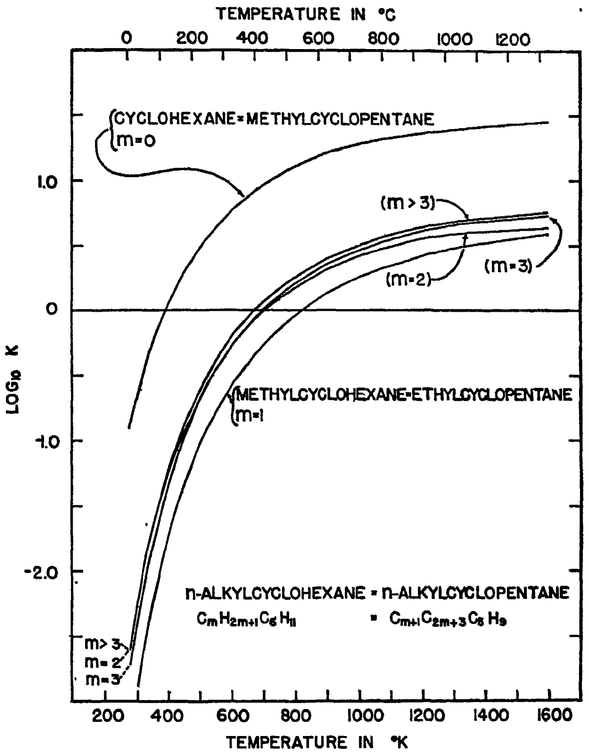


FIG. 48. Logarithm of the equilibrium constant for the reaction of conversion of normal alkylcyclohexanes to normal alkylcyclopentanes.

The scale of ordinates gives the value of the logarithm (to the base 10) of the equilibrium constant for the reaction of conversion of a given normal alkylcyclohexane to the corresponding normal alkylcyclopentane, in the gaseous state. The scale of abscissae gives the temperature in °K. and °C.

Fig. 50 gives a plot of the logarithm of the equilibrium constant, as a function of the temperature, for the following reactions of cyclization of 1-alkene mono-olefines to normal alkylcyclohexanes:

1-hexene (gas) = cyclohexane (gas) (70)
1-heptene (gas) = methylcyclohexane (gas) (71)
1-octene (gas) = ethylcyclohexane (gas) (72)
1-alkene (gas) = *n*-alkylcyclohexane (gas);
for 1-nonene and higher. (73)

IX. Conclusion

From the charts and tables presented in the foregoing pages one may obtain an overall picture of the chemical thermodynamic stability of, and values of the equilibrium constants of reactions involving, hydrocarbons of the classes of paraffins, mono-olefines, acetylenes, alkylbenzenes, alkylcyclopentanes, and alkylcyclohexanes in the gaseous state.

In the tables of the A.P.I. Research Project 44, values are given for all the normal alkyl members of each series, but for the isomers in each series values are given at present only to the following extent: paraffins, through the octanes; mono-olefines, through the hexenes; acetylenes, through the pentynes; alkylbenzenes, through the C_9H_{12} compounds; alkylcyclohexanes, through the C_8H_{16} compounds. Values are in process of calculation for the diolefine hydrocarbons, the styrenes and methylstyrenes, and the dimethylcyclopentanes. For complete tabulations of the various thermodynamic properties, readers are referred to the tables of the A.P.I. Research Project 44.

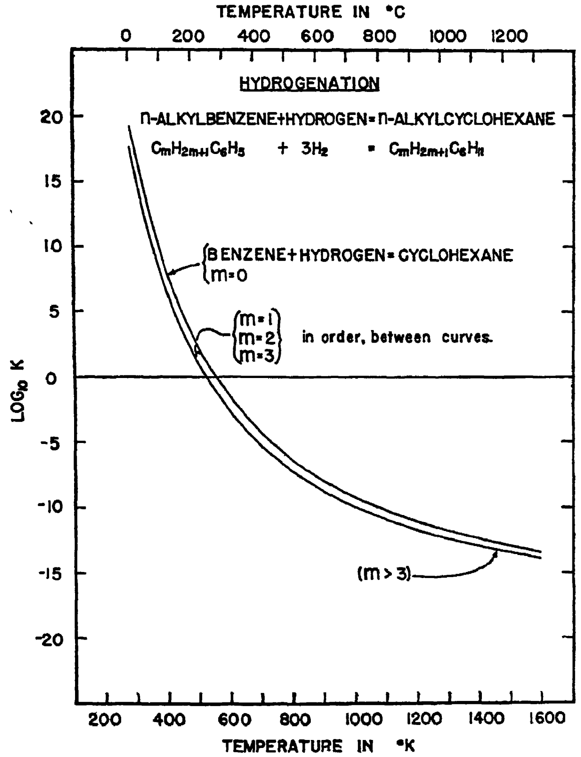


FIG. 49. Logarithm of the equilibrium constant for the reaction of hydrogenation of normal alkylbenzenes to normal alkylcyclohexanes.

The scale of ordinates gives the value of the logarithm (to the base 10) of the equilibrium constant for the reaction of hydrogenation of a given normal alkylbenzene to the corresponding normal alkylcyclohexane, in the gaseous state. The scale of abscissae gives the temperature in °K. and °C. The upper curve is that for the hydrogenation of benzene and the lower curve is for the hydrogenation of *n*-butylbenzene, *n*-pentylbenzene, and the higher normal alkylbenzenes. The curves for toluene, ethylbenzene, and *n*-propylbenzene are, in order, between the two curves.

In connexion with the distribution of the tables of physical and thermodynamic properties prepared by the A.P.I. Research Project 44, the American Petroleum Institute and the National Bureau of Standards have made the following arrangements:

(*a*) One complete set of the tables, together with supplements as prepared, will be supplied gratis to each Department of Chemistry, Chemical Engineering, Engineering, and Physics in universities and colleges,

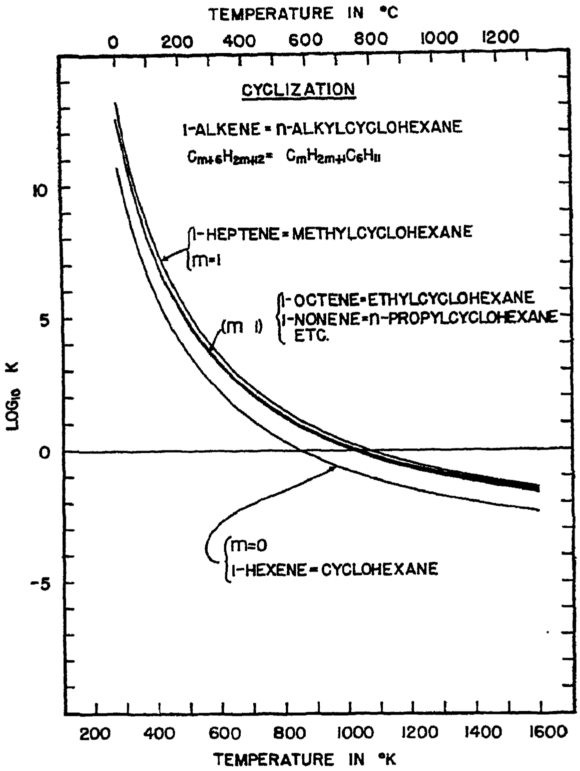


FIG. 50. Logarithm of the equilibrium constant for the reaction of cyclization of 1-alkene mono-olefines to normal alkylcyclohexanes. The scale of ordinates gives the value of the logarithm (to the base 10) of the equilibrium constant for the reaction of cyclization of a given 1-alkene mono-olefine to the corresponding normal alkylcyclohexane, in the gaseous state. The scale of abscissae gives the temperature in °K. and °C. The value for the formation of ethylcyclohexane, *n*-propylcyclohexane, and the higher normal alkylcyclohexanes all fall within the width of the heavy line.

with the compliments of the American Petroleum Institute and the National Bureau of Standards, on application to the National Bureau of Standards.

(*b*) Up to 10 copies of each table prepared will be supplied gratis to each of the supporters of the research fund of the American Petroleum Institute, on application to the Institute.

(*c*) Additional sets of the tables may be obtained by individuals, companies, and institutions, on order from the American Petroleum Institute at 5 cents per sheet in complete sets only.

X. Publications of the American Petroleum Institute Research Project 44 at the National Bureau of Standards

1. Application of Polya's Theorem to Optical, Geometrical, and Structural Isomerism. WILLIAM J. TAYLOR. *J. Chem. Phys.* **11**, 532 (1943).
2. The Calory and the Joule in Thermodynamics and Thermochemistry. EUGENE F. MUELLER and FREDERICK D. ROSSINI. *Am. J. Phys.* **12**, 1 (1944).
3. Theoretical Analysis of Certain Time-temperature Freezing and Melting Curves as applied to Hydrocarbons. WILLIAM J. TAYLOR and FREDERICK D. ROSSINI. *J. Res. Nat. Bur. Standards,* **32**, 197 (1944).
4. Heats of Formation and Combustion of 1,3-Butadiene and Styrene. EDWARD J. PROSEN and FREDERICK D. ROSSINI. *J. Res. Nat. Bur. Standards,* **34**, 59 (1945).
5. Heats, Free Energies, and Equilibrium Constants of Some Reactions involving O_2, H_2, H_2O, C, CO, CO_2 and CH_4. DONALD D. WAGMAN, JOHN E. KILPATRICK, WILLIAM J. TAYLOR, KENNETH S. PITZER, and FREDERICK D. ROSSINI. *J. Res. Nat. Bur. Standards,* **34**, 143 (1945).
6. Free Energies and Equilibria of Isomerization of the 18 Octanes. EDWARD J. PROSEN, KENNETH S. PITZER, and FREDERICK D. ROSSINI. *J. Res. Nat. Bur. Standards,* **34**, 255 (1945).
7. Heats of Combustion and Formation of the Paraffin Hydrocarbons at 25° C. EDWARD J. PROSEN and FREDERICK D. ROSSINI. *J. Res. Nat. Bur. Standards,* **34**, 263 (1945).
8. Heats and Free Energies of Formation of the Paraffin Hydrocarbons in the Gaseous State, to 1,500° K. EDWARD J. PROSEN, KENNETH S. PITZER, and FREDERICK D. ROSSINI. *J. Res. Nat. Bur. Standards,* **34**, 403 (1945).
9. Method for calculating the Properties of Hydrocarbons and its Application to the Refractive Indices, Densities, and Boiling Points of the Paraffin and Mono-olefine Hydrocarbons. WILLIAM J. TAYLOR, JOAN M. PIGNOCCO, and FREDERICK D. ROSSINI. *J. Res. Nat. Bur. Standards,* **34**, 413 (1945).
10. Method of Lagrangian Curvilinear Interpolation. WILLIAM J. TAYLOR. *J. Res. Nat. Bur. Standards,* **35**, 151 (1945).
11. Vapour Pressures and Boiling Points of some Paraffin, Alkylcyclopentane, Alkylcyclohexane, and Alkylbenzene Hydrocarbons. CHARLES B. WILLINGHAM, WILLIAM J. TAYLOR, JOAN M. PIGNOCCO, and FREDERICK D. ROSSINI. *J. Res. Nat. Bur. Standards,* **35**, 219 (1945).
12. Heats, Equilibrium Constants, and Free Energies of Formation of the Acetylene Hydrocarbons through the Pentynes, to 1,500° K. DONALD D. WAGMAN, JOHN E. KILPATRICK, KENNETH S. PITZER, and FREDERICK D. ROSSINI. *J. Res. Nat. Bur. Standards,* **35**, 467 (1945).
13. Heats of Formation, Hydrogenation, and Combustion of the Mono-olefine Hydrocarbons through the Hexenes, and of the Higher 1-Alkenes, in the Gaseous State, at 25° C. EDWARD J. PROSEN and FREDERICK D. ROSSINI. *J. Res. Nat. Bur. Standards,* **36**, 269 (1946).
14. Heats of Combustion and Formation at 25° C. of the Alkylbenzenes through $C_{10}H_{14}$ and of the Higher Normal Monoalkylbenzenes. EDWARD J. PROSEN, WALTER H. JOHNSON, and FREDERICK D. ROSSINI. *J. Res. Nat. Bur. Standards,* **36**, 455 (1946).
15. Heats, Equilibrium Constants, and Free Energies of Formation of the Mono-olefine Hydrocarbons. JOHN E. KILPATRICK, EDWARD J. PROSEN, KENNETH S. PITZER, and FREDERICK D. ROSSINI. *J. Res. Nat. Bur. Standards,* **36**, 559 (1946).
16. Heats of Formation and Combustion of the Normal Alkylcyclopentanes and Cyclohexanes, and the Increments per CH_2 Group for Several Homologous Series of Hydrocarbons. EDWARD J. PROSEN, WALTER H. JOHNSON, and FREDERICK D. ROSSINI. *J. Res. Nat. Bur. Standards,* **37**, 51 (1946).
17. Heats, Equilibrium Constants, and Free Energies of Formation of the Alkylbenzenes. WILLIAM J. TAYLOR, DONALD D. WAGMAN, MARY G. WILLIAMS, KENNETH S. PITZER, and FREDERICK D. ROSSINI. *J. Res. Nat. Bur. Standards,* **37**, 95 (1946).
18. Heat Content, Free Energy Function, Entropy, and Heat Capacity of Ethylene, Propylene, and the Four Butenes, to 1,500° K. JOHN E. KILPATRICK and KENNETH S. PITZER. *J. Res. Nat. Bur. Standards,* **37**, 163 (1946).
19. Upper and Lower Bounds to Rayleigh's Frequency for a Vibrating System. WILLIAM J. TAYLOR. *J. Chem. Phys.* **14**, 570 (1946).
20. The Entropies and Related Properties of Branched Paraffin Hydrocarbons. KENNETH S. PITZER and JOHN E. KILPATRICK. *Chem. Rev.* **39**, 435 (1946).
21. The Thermodynamics of Styrene and its Methyl Derivatives. CHARLES W. BECKETT and KENNETH S. PITZER. *J. Am. Chem. Soc.* **68**, 2213 (1946).
22. Vibrational Frequencies of Semirigid Molecules: A General Method and Values for Ethylbenzene. WILLIAM J. TAYLOR and KENNETH S. PITZER. *J. Res. Nat. Bur. Standards,* **38**, 1 (1947).
23. Normal Co-ordinate Analysis of the Vibrational Frequencies of Ethylene, Propylene, cis-2-butene, trans-2-butene, and Isobutene. JOHN E. KILPATRICK and KENNETH S. PITZER. *J. Res. Nat. Bur. Standards,* **38**, 191 (1947).
24. Average Square Length and Radius of Unbranched Long-chain Molecules with Restricted Internal Rotation. WILLIAM J. TAYLOR (1947).
25. Average Square Length and Radius of Normal Paraffin Hydrocarbon Molecules. WILLIAM J. TAYLOR (1947).
26. Tautomerism in Cyclohexane Derivatives: Reassignment of Configuration of the 1,3-Dimethylcyclohexanes. KENNETH S. PITZER and CHARLES W. BECKETT (1947).
27. Heats of Formation and Isomerization of the Eight C_8H_{16} Alkylcyclohexanes. EDWARD J. PROSEN, WALTER H. JOHNSON, and FREDERICK D. ROSSINI (1947).

28. The Thermodynamic Properties and Molecular Structure of Cyclohexane, Methylcyclohexane, Ethylcyclohexane, and the Seven Dimethylcyclohexanes. Charles W. Beckett, Kenneth S. Pitzer, and Ralph Spitzer (1947).
29. Thermodynamics and Molecular Structure of Cyclopentane. John E. Kilpatrick, Kenneth S. Pitzer, and Ralph Spitzer (1947).
30. Technical and Scientific Services of the National Bureau of Standards for the Petroleum Industry. Frederick D. Rossini. Division of Chemical Education and Division of Petroleum Chemistry, American Chemical Society, Atlantic City, New Jersey, April, 1947.
31. Heats, Equilibrium Constants, and Free Energies of Formation of the Alkylcyclopentanes and Alkylcyclohexanes. John E. Kilpatrick, Charles W. Beckett, Helene G. Werner, Kenneth S. Pitzer, and Frederick D. Rossini (1947).
32. Chemical Thermodynamic Properties of Hydrocarbons. Frederick D. Rossini. For vol. V of *Science of Petroleum.*

HIGH-PRESSURE VAPOUR–LIQUID EQUILIBRIA IN CYCLING OPERATIONS

By DONALD L. KATZ and MICHAEL J. RZASA

University of Michigan

VAPOUR–LIQUID equilibria encountered in the production of crude oil and natural gas usually involve high pressures as compared to those found in normal petroleum refineries. The more volatile components of the naturally occurring systems in petroleum reservoirs are paraffinic compounds, with methane the predominant constituent. The high pressures and the compositions of the natural gases involved in the producing industry require an approach to the prediction of vapour-liquid equilibria differing from that used for the usual distillation process.

A cycling operation [1, 1945; 13, 1943; 22, 1945] presents most of the examples for high-pressure vapour–liquid equilibria in the producing industry. Fig. 1 shows diagrammatically the gas reservoir and cycling plant. High-pressure natural gas is produced from wells, processed to recover desirable liquid hydrocarbons, and the stripped lean gas returned to the reservoir. In this operation there are three types of mixtures involved which are worthy of distinction when considering vapour–liquid equilibria.

The high-pressure natural gas in the reservoir may be in equilibrium at the time of discovery with a crude-oil layer below the gas phase. Also, the high-pressure gas may precipitate a condensate in the reservoir due to pressure reduction by gas withdrawal. This case of vapour–liquid equilibria involves pressures from 2,000 to 10,000 lb. per sq. in. at temperatures from about 120° to 300° F. As the natural gas bearing condensate is produced from the well, it may be divided into a gas and liquid phase in a separator. This second case covers natural gas-condensate systems at pressures of 500 to 3,000 lb. per sq. in. at temperatures from about 50° to 150° F. The removal of liquid hydrocarbons from natural gas in absorbers presents the third type of equilibria for systems composed of natural gas and absorber oil at pressures of 400 to 2,500 lb. and temperatures around 100° F.

The distinguishing feature of these high-pressure operations over conventional processes at 200 to 600 lb. per sq. in. is the increase in volatility of the higher boiling components with increasing pressure. This effect of pressure on the volatility is associated with critical phenomena and retrograde condensation [9, 1940]. The foundation for the behaviour of reservoir fluids at high pressure was laid by

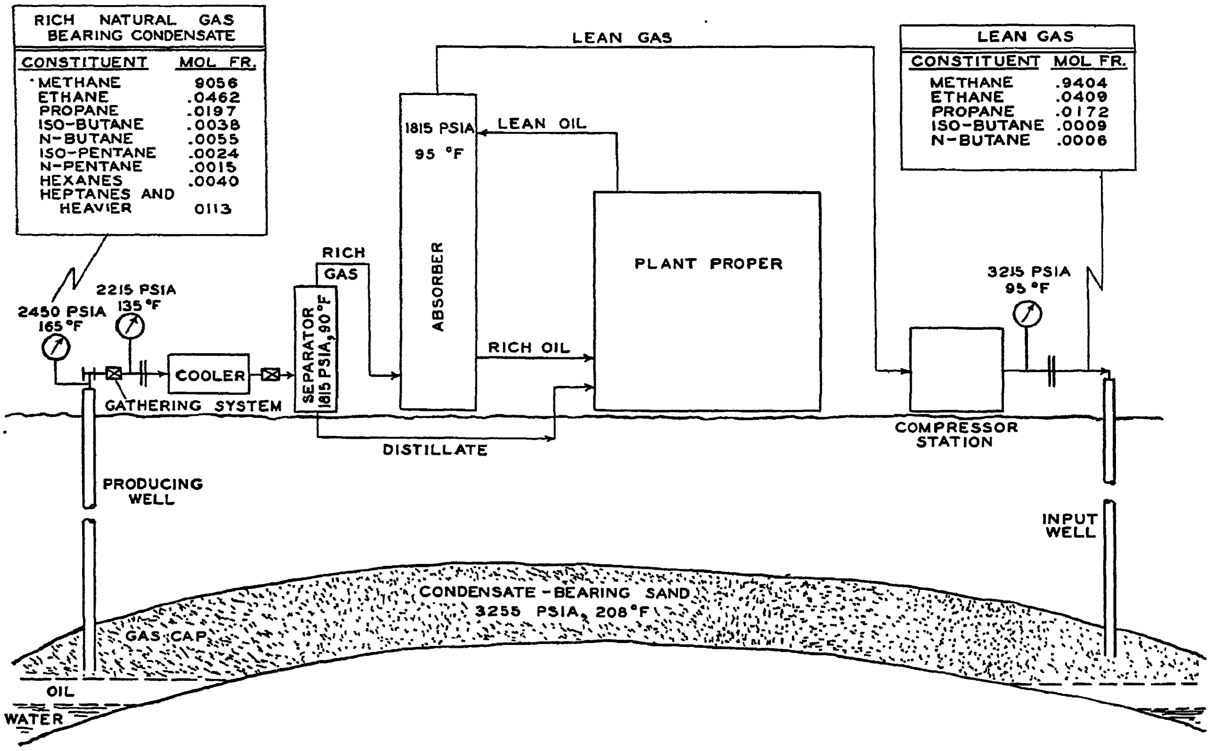


FIG. 1. Diagrammatic sketch of cycling plant and natural gas reservoir.

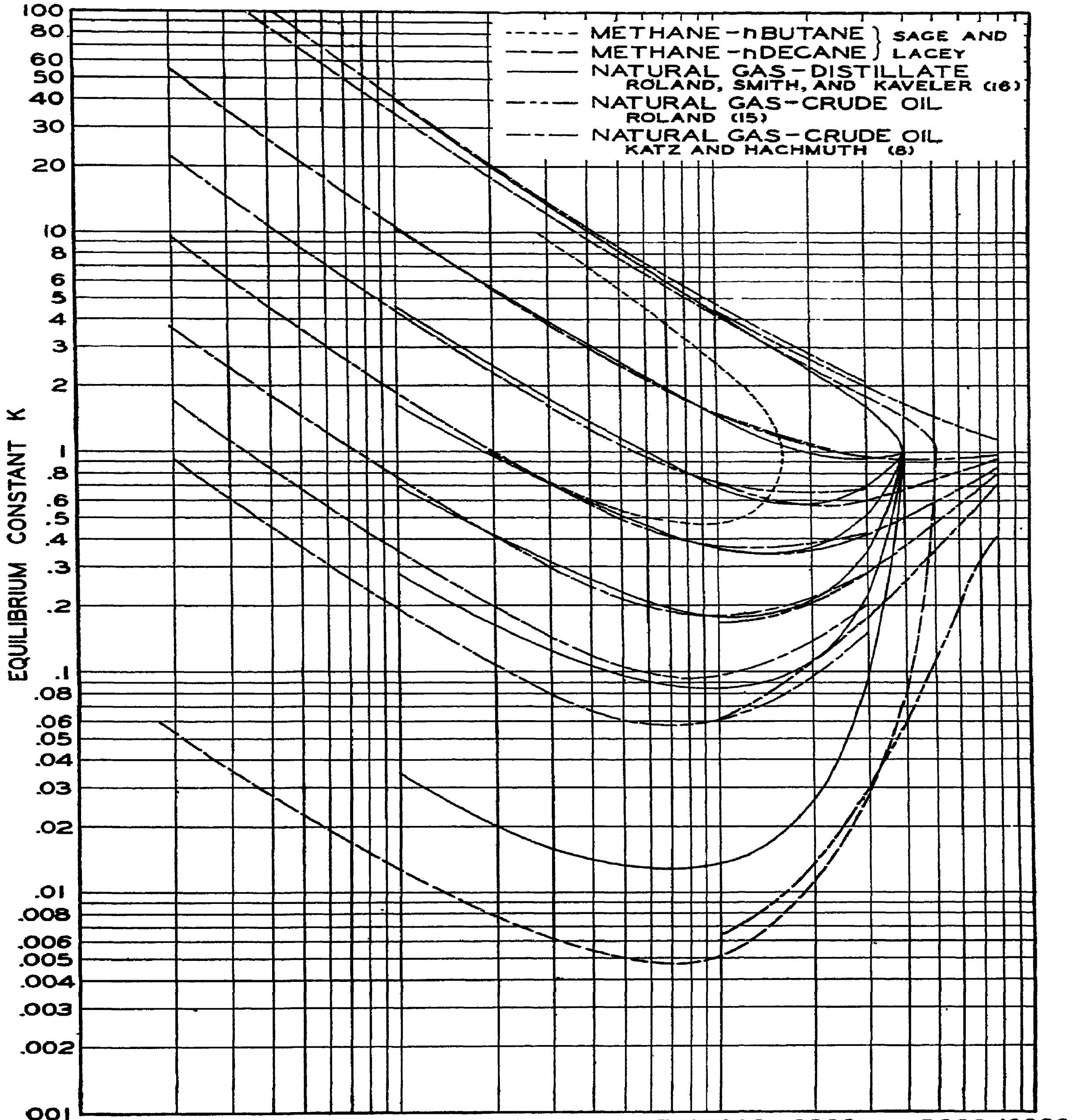


FIG. 2. Phase diagram of a synthetic natural gas–natural gasoline mixture (11).

the physicists and physical chemists who investigated in the nineteenth century the behaviour of simple systems in the critical region [10, 1946].

This chapter presents the nomenclature and background for predicting vapour–liquid equilibria. The data in the literature on complex mixtures related to fluids handled in cycling operations are reviewed as the basis for vapour–liquid equilibria calculations. Up to pressures of about 3,000 lb. per sq. in. these calculations are generally satisfactory, while at pressures of 3,000 to 10,000 lb. per sq. in. the procedures become less reliable. Present concepts are presented for predicting the behaviour of hydrocarbon mixtures under these extreme conditions.

Phase Nomenclature

For each mixture, either binary or complex, a phase diagram may be determined. Fig. 2 shows experimental data on a synthetic mixture of natural gas and natural gasoline [11, 1942]. The composition for this mixture is not representative of natural gas-condensate reservoir material, but the phase diagram is qualitatively correct for the study of such systems. Therefore it will be used for discussing the nomenclature and phase behaviour of reservoir fluids. Reports on the phase relations of mixtures from condensate wells indicate similar behaviour [2, 1941; 3, 1944; 12, 1946; 14, 1945; 23, 1946].

In Fig. 8, curve *AFC* represents the bubble-points for the mixture and curve *CQOMDKB* represents the dew-points. Outside these curves the mixture is in a single phase and within the area the mixture separates into two phases at equilibrium. The critical point *C* is the junction between the bubble-point and the dew-point curves.

The mixture at *E* is in a single phase. As the pressure is reduced isothermally to *F*, bubbles of vapour will appear until at *G* the system is 60 vol. % vapour and 40 vol. % liquid. Likewise, a single phase at *H* forms a small amount of liquid or 'dew' when compressed isothermally to *K*.

A reservoir may contain a mixture having a phase diagram similar to that shown in Fig. 2. If the initial condition for the reservoir were at point *M* (2,340 lb. per sq. in., 208° F.) the mixture would be at its upper dew-point at that temperature. This condition would correspond to that of a gas phase above an oil layer in the reservoir in which the phase diagram is for the gas phase only. A reduction in reservoir pressure to 1,700 lb. per sq. in. at 208° F. would bring the original gas mixture in the reservoir to point *N*, at which condition the system would be composed of 6·9 % by volume liquid and 93·1 % by volume gas. This condensation by isothermal reduction in pressure is called retrograde condensation [9, 1940]. Further decreases in pressure bring the system to a single phase at *K*, the lower dew-point, by normal vaporization. The reverse path from *K* to *N* represents normal condensation, while retrograde vaporization occurs over the isothermal path from *N* to *M*.

If the original reservoir gas mixture were at *L*, it would be in a single phase and no phase change would accompany a pressure reduction until point *M* was reached. Reservoir temperatures above the point *D* would indicate that condensation would not occur during isothermal pressure changes in the reservoir.

Temperature reduction on the mixture originally at *L* will cause normal condensation to begin at *O*, and reach a maximum at *P*. Further isobaric decrease in temperature will result in retrograde vaporization as point *Q* is approached.

Most actual condensate reservoir systems are either on or somewhat above the upper dew-point curve for their system. Some reservoir fluids are at a position on their diagram such that only a small quantity of condensate will form by pressure reduction, while others, usually the reservoirs with a high liquid yield, will form considerable liquid by retrograde condensation [12, 1946].

Vapour–Liquid Equilibria in Binary Systems

Binary systems including methane as the more volatile component provide the fundamental data for understanding high-pressure vapour-liquid equilibria. Fig. 3 presents the phase diagrams and critical locus for the methane–butane system from Sage, Hicks, and Lacey [18, 1940].

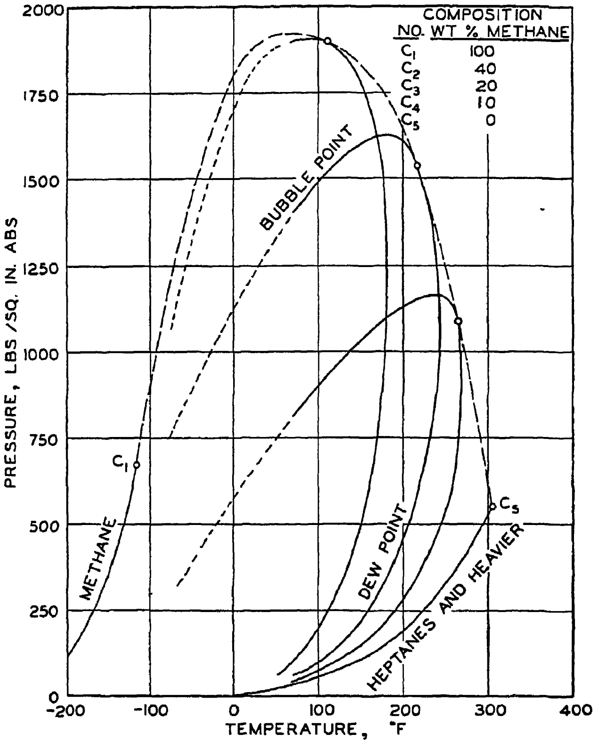


FIG. 3. Phase diagrams and critical locus of the methane-*n*-butane system (18).

The effect of composition of the mixture on the pressures and temperatures for the two-phase area should be noted. Each reservoir fluid has a phase diagram corresponding to its composition just as illustrated for the particular binary mixtures. In general, mixtures containing the higher concentration of methane will have the lower critical temperature with a shift in the slope of the bubble dew-point curve adjacent to the critical. The diagram of Fig. 2 corresponds to a methane-butane mixture containing more than 40 weight % methane which has its critical temperature at about 30° F.

Fig. 4 presents the equilibrium constants [18, 1940] for the methane-butane system at selected temperatures. Equilibrium constants (mol fraction in vapour divided by mol fraction in liquid [20, 1932]) in a given binary system are a function of pressure and temperature only. The compositions of the vapour and liquid become identical as a mixture is compressed isothermally to the critical pressure at the critical temperature. As the compositions become identical the equilibrium constants approach unity. The constant for the more volatile component decreases while the constant for the less volatile component increases to reach unity. The pressures at which the constants converge to unity are the critical pressures corresponding to the critical temperatures, as indicated by the critical locus of Fig. 3.

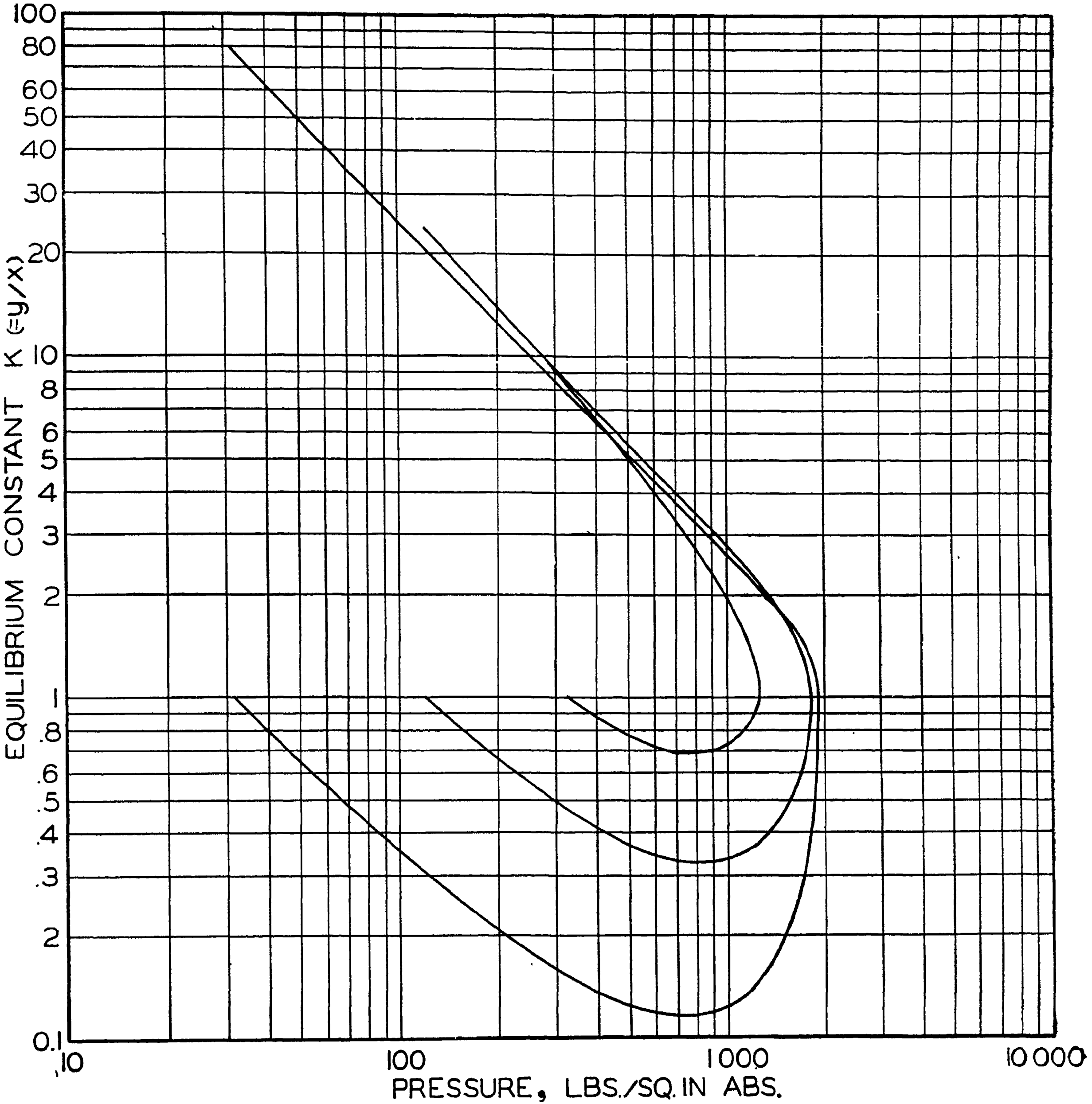


Fig. 4. Equilibrium constants at selected temperatures for the methane-*n*-butane system (18).

The critical loci of binary hydrocarbon systems with methane the volatile constituent are shown in Fig. 5. The greater the spread in volatility of the two components, the higher is the pressure for the critical locus, and hence the systems exist as two phases at higher pressures. The calculated critical locus for methane and the compound, $C_{32}H_{66}$ (mol. wt. 450, n.b.p. 828° F.), demonstrates that hydrocarbon mixtures containing methane may well exist in the two-phase region at pressures to 20,000 lb. per sq. in.

Vapour–Liquid Equilibria for Complex Mixtures

The phase-equilibria information desired by the engineer for naturally occurring mixtures are the state of the mixture (fraction vapour and liquid) at specified temperatures and pressures and the compositions of the coexisting vapour and liquid phases. For binary systems the diagrams of Fig. 3 can present this information if enough mixtures are included. For complex mixtures containing from 5 to 25 components it is impossible to represent the relations and compositions by such phase diagrams.

The equilibrium constants of Fig. 4 may be used to predict the bubble-point, dew-point, or fraction vaporized, and the phase compositions for any selected methane-butane system. For complex systems the same calculations of bubble-point, dew-point, &c., may be made for a given mixture, by use of equilibrium constants [7, 1938]. At low pressures the equilibrium constants for the constituents in naturally occurring mixtures are substantially ideal and apply to any natural gas, distillate, or crude oil with little dependence on composition, except for the methane [6, 1945; 17, 1941]. However, at high pressures the constants for binary systems are shown to depend on the critical pressure corresponding to a given critical temperature. Regardless of the composition of a binary mixture, the equilibrium constants at a temperature and pressure are those obtained for the mixture which has its critical temperature at the equilibrium temperature. For complex mixtures it would seem that the constants depend on the temperature, pressure, and the pressure at which the constants converge to unity [5, 1945].

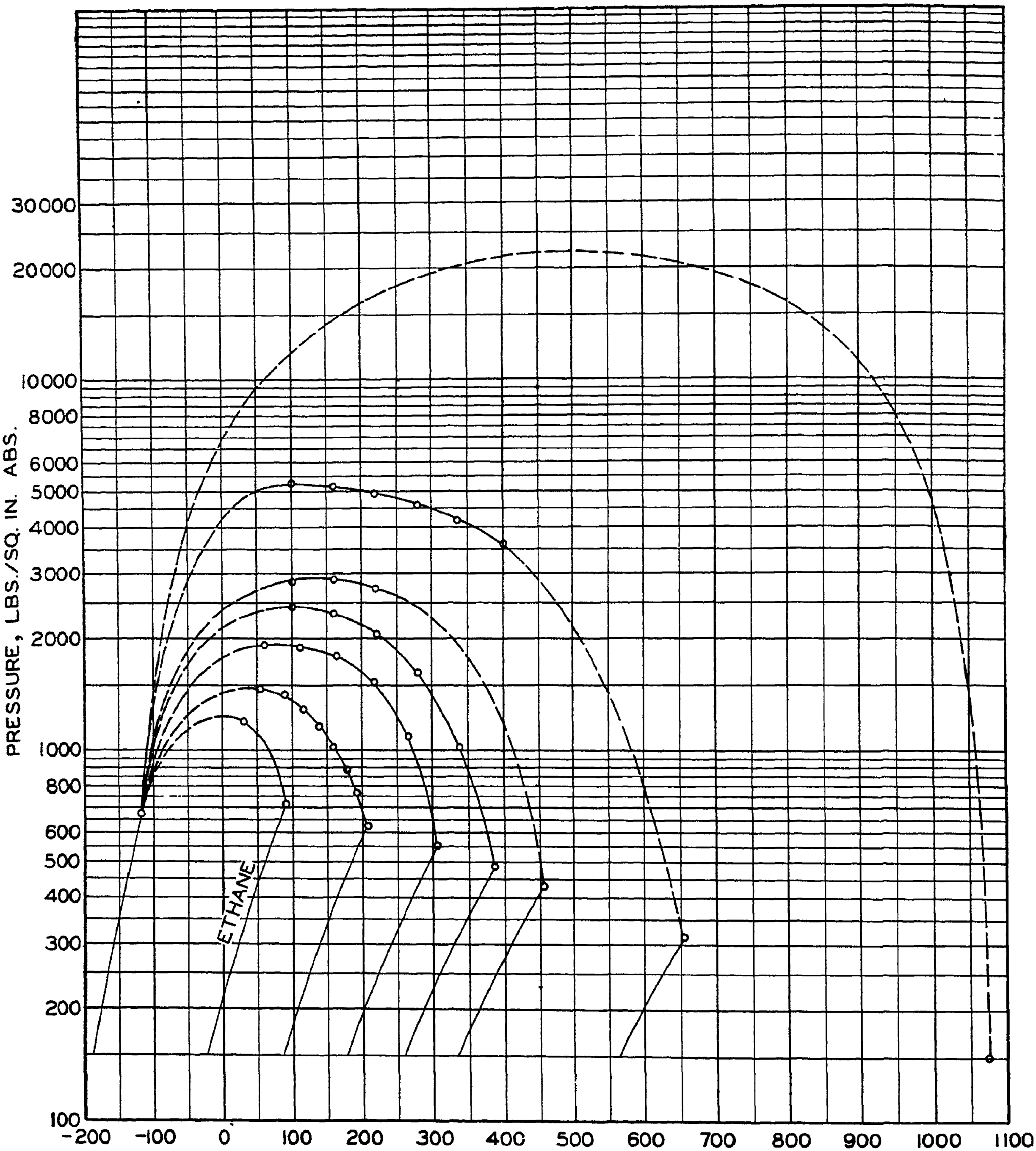


FIG. 5. Critical loci of binary hydrocarbon systems containing methane.

The equilibrium constants for a complex mixture at its critical temperature converge to unity at the critical pressure.

However, the usual field mixture is not at its critical temperature and then the question arises, What is the convergence pressure? For binary systems it would be the critical pressure for the particular binary mixture which has its critical temperature at the temperature for which the constants are desired. Unfortunately no critical data are available for mixtures above about 5,300 lb. per sq. in. and methods of predicting critical temperatures and pressures from compositions are inadequate for mixtures having critical pressures of 3,000–25,000 lb. per sq. in. [11, 1942; 19, 1937].

Using the best critical pressures and temperatures that could be predicted, the critical locus for a complex mixture has been calculated treating it as a binary system of natural gas and oil or of methane and remainder of system [4, 1946]. This critical locus should then be the convergence pressure for the constants in the complex mixture. Experimental data to test this binary theory as applied to complex mixtures showed that different gas-oil ratios of a given oil-gas system when compressed to high pressures gave vastly different equilibrium constants and different convergence pressures [21, 1944].

In addition to the difficulty of predicting convergence pressures, the behaviour of experimental equilibrium constants at high pressures, above 4,000 lb. [15, 1945; 21, 1944; 24, 1941], has indicated that the constants for complex mixtures approach unity tangentially rather than in the manner shown in Fig. 4. Fig. 6 from Roland [15, 1945] shows experimental data on a crude oil–natural gas system. Further progress in understanding phase equilibria for complex mixtures will take the direction of obtaining equilibrium constants for a given system for which the phase and critical relations are known.

TABLE I

Reported Equilibrium Constants for Complex Systems

System	*Temperature* °*F.*	*Pressure lb./sq. in. abs.*	*Authors*	*Reference*
Natural gas–Crude oil .	40–200	14·7–3,400	Katz and Hachmuth	8
Natural gas–Distillate .	40–200	200–4,000	Roland, Smith, and Kaveler	16
Hydrocarbons–Absorber oil.	33–180	100–5,000	Webber	24
Natural gas–Crude oil .	35–250	1,000–8,220	Standing and Katz	21
Quintary paraffin systems .	100	200–2,000	Hanson and Brown	5
Natural gas–Crude oil .	120 and 200	1,000–10,000	Roland	15

Table I lists equilibrium data reported for complex mixtures. Fig. 7 is a plot of equilibrium constants at 200° F.

To obtain a single series of constants for complex mixtures with increasing pressure such as shown in Fig. 6, it is necessary to use the same overall composition for each equilibrium. Some of the data reported used arbitrary ratios of a gas and a liquid to obtain successive mixtures in the equilibrium cell. At pressures considerably below the critical or apparent convergence pressure the influence of composition is small. Thus at pressures from 2,000 to 3,000 lb. per sq. in. for the Oklahoma City crude oil and gas mixtures [8, 1937] the constants obtained formed a relatively smooth curve with increasing pressure at constant temperature even though the overall equilibrium mixture was not maintained exactly the same. Unreported data by Roland [15, 1945] gave a bad scattering of points with increasing pressure when the mixture of natural gas and crude charged to the equilibrium cell was not held constant within close limits. The data by Webber [24, 1941] did not hold constant composition, while Standing and Katz [21, 1944], Roland, Smith, and Kaveler [16, 1941], and Roland [15, 1945] obtained data on constant composition systems.

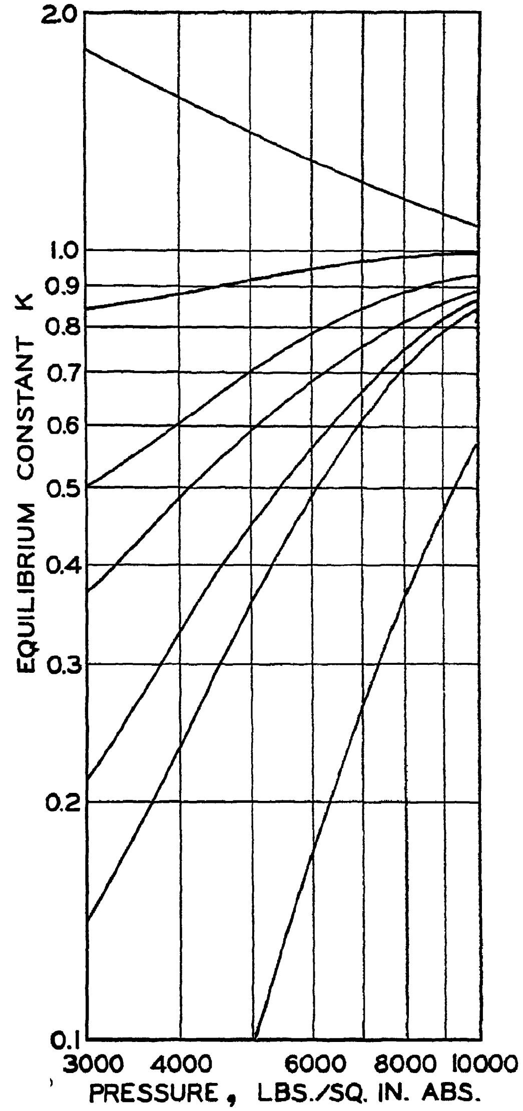


FIG. 6. Equilibrium constants at 120° F. for a natural gas–crude oil mixture (15).

Before it became evident that the equilibrium constants for complex mixtures (Fig. 6) did not converge towards unity in the same manner as binary systems, a principle for predicting convergence pressure was developed. For a given complex mixture *A* which will divide into equilibrium liquid *B* and equilibrium vapour *C* at T_1 and P_1, only one set of equilibrium constants will apply at T_1 and P_1. If equilibrium liquid *B* were chosen as a system, the equilibrium constants at T_1 would be the same at P_1 as for system *A*. Likewise for system *C* the equilibrium constants at T_1 and P_1 are the same as for systems *A* and *B*. All mixtures of *B* and *C* will have these constants at T_1 and P_1.

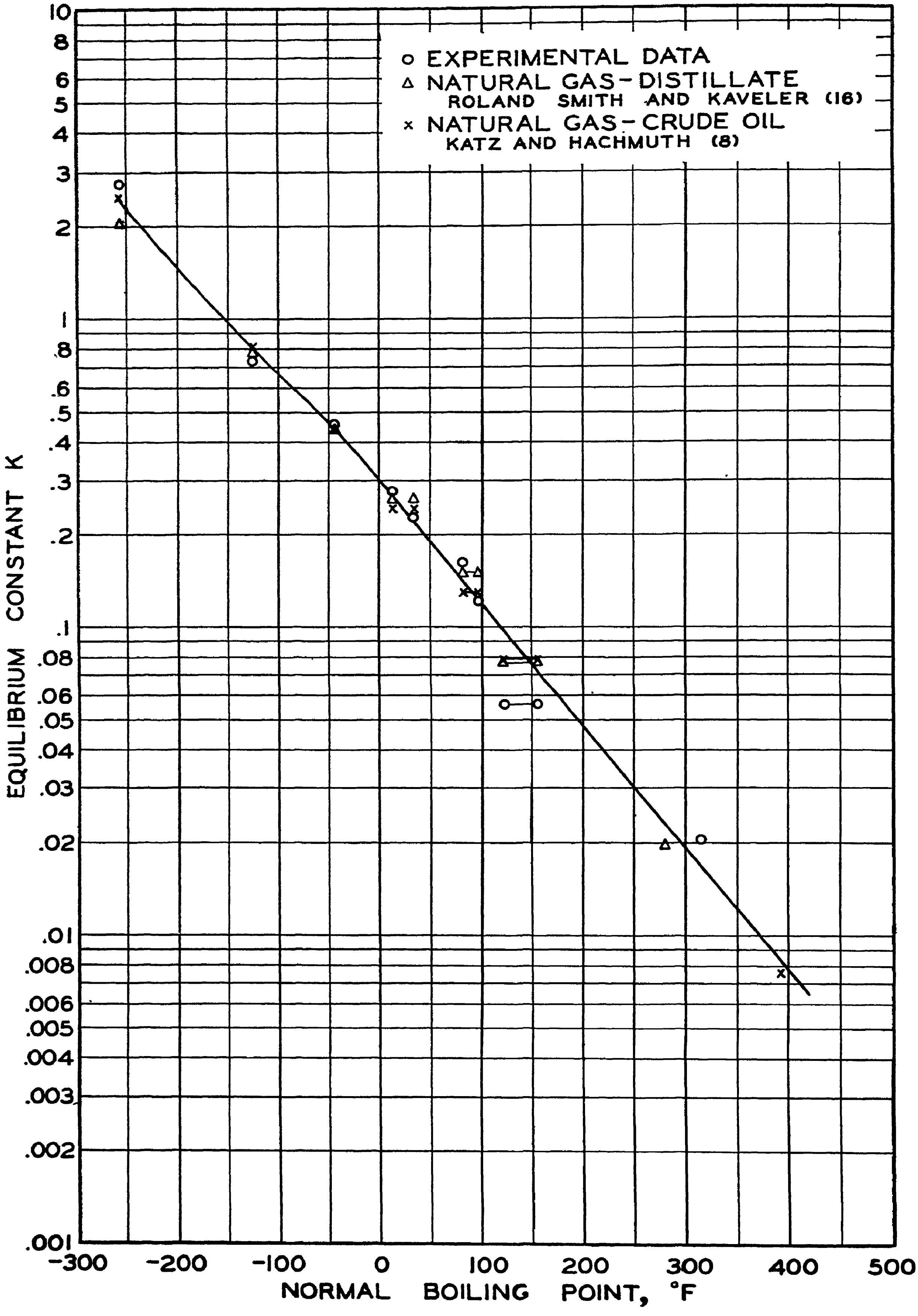


Fig. 7. Equilibrium constants at 200° F. for various systems.

Some mixture of B and C must have T_1 as its critical temperature and P_2 as its critical pressure. Pressure P_2 then becomes the convergence pressure for the mixture of B and C which has T_1 as its critical temperature.

An observation verified by experimental data [15, 1945] is that the equilibrium constants for systems A, B, and C at T_1 are the same for all pressures below P_1. The presence of asphaltic components may invalidate this concept.

The following method is suggested for calculating vapour–liquid equilibria for some mixture D at T_2 and P_3. Select a convergence pressure, find equilibrium constants at T_2 and P_3, and compute the vapour E and liquid F compositions. Mix vapour E and liquid F so that the calculated critical temperature is T_2. Then P_4, the critical pressure for mixture of E and F which has a critical temperature of T_2, becomes the convergence pressure for computing equilibrium constants at P_3 and lower pressures. Using this convergence pressure to obtain the equilibrium constants, a new calculation for vapour E and liquid F may be made if necessary.

Until such time as methods for computing critical temperatures and pressures for complex mixtures whose critical pressures are from 4,000 to 20,000 lb. per sq. in. are reliable, there is little opportunity to test this procedure.

Prediction of Vapour–Liquid Equilibria for Cycling Operations

The three kinds of systems occurring in cycling operations for which equilibrium data are required are the natural gas-condensate, natural gas-condensate-absorber oil, and the reservoir fluid.

The effluent from a condensate well passing into a separator at 500–3,000 lb. per sq. in. normally divides into a liquid and a vapour. This system is characterized by the gas–liquid ratio and the gravity of the liquid resulting from flashing the separator liquid to atmospheric pressure. Another measure of the type of constants to be used for the system is the molecular weight of the heptanes and heavier fraction in the liquid. Roland, Smith, and Kaveler used a liquid of 57·5° API. with a molecular weight of 119·5 for heptanes and heavier in the liquid. Their data indicated little change in equilibrium constants with changes in composition—which behaviour is not true for mixtures having heptanes and heavier fraction of higher molecular weight such as crude oil. For normal condensate well effluents whose separator liquids at atmospheric pressure are 55° API. or higher or whose heptanes and heavier fraction has a molecular weight in the liquid below about 120, the constants of Roland, Smith, and Kaveler are satisfactory. Plots of their data as log K versus temperature, lines of constant pressure are convenient for use.

If the liquid has a lower API. gravity or the heptanes and heavier a higher molecular weight, the equilibrium constants on constant temperature plots of log K versus log pressure will probably converge towards pressures of 5,000–7,000 lb. per sq. in. rather than those given by the data. The constant for the heptanes and heavier fraction should be obtained by plotting log K versus normal boiling-point or molecular weight at constant temperature and pressure.

For absorbers the primary part of the mixture for controlling the constants is the absorber oil. Molecular weights of 180 to 250 for absorber oil give it the same average properties as many crude oils—the difference being in the narrower boiling range. Mixtures in absorbers will give equilibrium constants having higher apparent convergence pressures than natural gas-condensate systems having low molecular weight for the heptanes and heavier fraction. For calculations the data of Katz and Hachmuth suitably plotted are satisfactory for absorbers for pressures up to 3,000 lb. per sq. in. The data of Webber will assist in obtaining the constant for the oil. His data also show that mixtures containing more intermediate constituents (butanes, pentanes, or hexanes) have lower apparent convergence pressures than mixtures comprised primarily of methane and absorber oil. At 2,000 lb. per sq. in. and 100° F. the crude oil–natural gas data give a methane K of 2·63, while the natural gas–absorber oil give Ks from 2·08 to 2·87 depending on the quantity of intermediate constituent present. At 100° F. the constituents propane and heavier will all have a lower K when the quantity of intermediate constituents is low and convergence pressure high. The best constants will be found by considering the composition of the system in question in relation to the data available, using the characteristics of the absorber oil and the distribution of constituents as guides.

Intermediate between the above gas-condensate and gas-absorber oil mixtures are those mixtures with heptanes and heavier fractions with molecular weights between 120 and 180. Table II gives a well effluent from a gas-condensate reservoir. The heptanes and heavier fraction in the liquid has a molecular weight of 159·5 and the condensate at atmospheric pressure a gravity of 47° API. Fig. 8 is a comparison between the experimental equilibrium constants and those predicted from literature data [16, 1941; 8, 1937] at the operating temperature and pressure of the field separator.

The experimental equilibrium constant for methane is higher than would be predicted from Katz and Hachmuth or Roland, Smith, and Kaveler. The method for plotting the heptanes and heavier fractions is to find the normal boiling-point [19, 1937] corresponding to the average molecular weight and density of the heptanes and heavier fraction in the liquid and vapour. At 2,200 lb. per sq. in. and 100° F. the molecular weight of the heptanes and heavier fraction in the vapour was taken as 110 and the specific gravity as 0·72.

Table II gives the comparison between experimental and calculated phase compositions at 2,200 lb. per sq. in. and 101° F. The calculated liquid content in the separator was 0·91 gal. per min. while the experimental value was 0·95 gallons liquid per thousand standard cu. ft. of gas. Differences of about 10% of the amounts occur for the calculated and experimental concentrations of methane and the heptanes and heavier fractions in the separator liquid.

For reservoirs, equilibrium constants are often required at pressures approaching the convergence pressure. Computation of the phase compositions for a known mixture at a given temperature and pressure may be made by arbitrarily selecting equilibrium constants from data reported for a similar system. The phase compositions so calculated may be compared with the phase compositions of the data providing the equilibrium constants. If significant differences exist, one may wish to select a new set of equilibrium constants based on other data or intermediate between two sets of data.

When further information is available on computing critical pressures, on the nature of the convergence of the Ks for naturally occurring systems, and on the influence of asphalt, it may be possible to compute a convergence pressure by the procedure outlined. Continued studies of phase equilibria at reservoir conditions are necessary to arrive at satisfactory procedures of calculation.

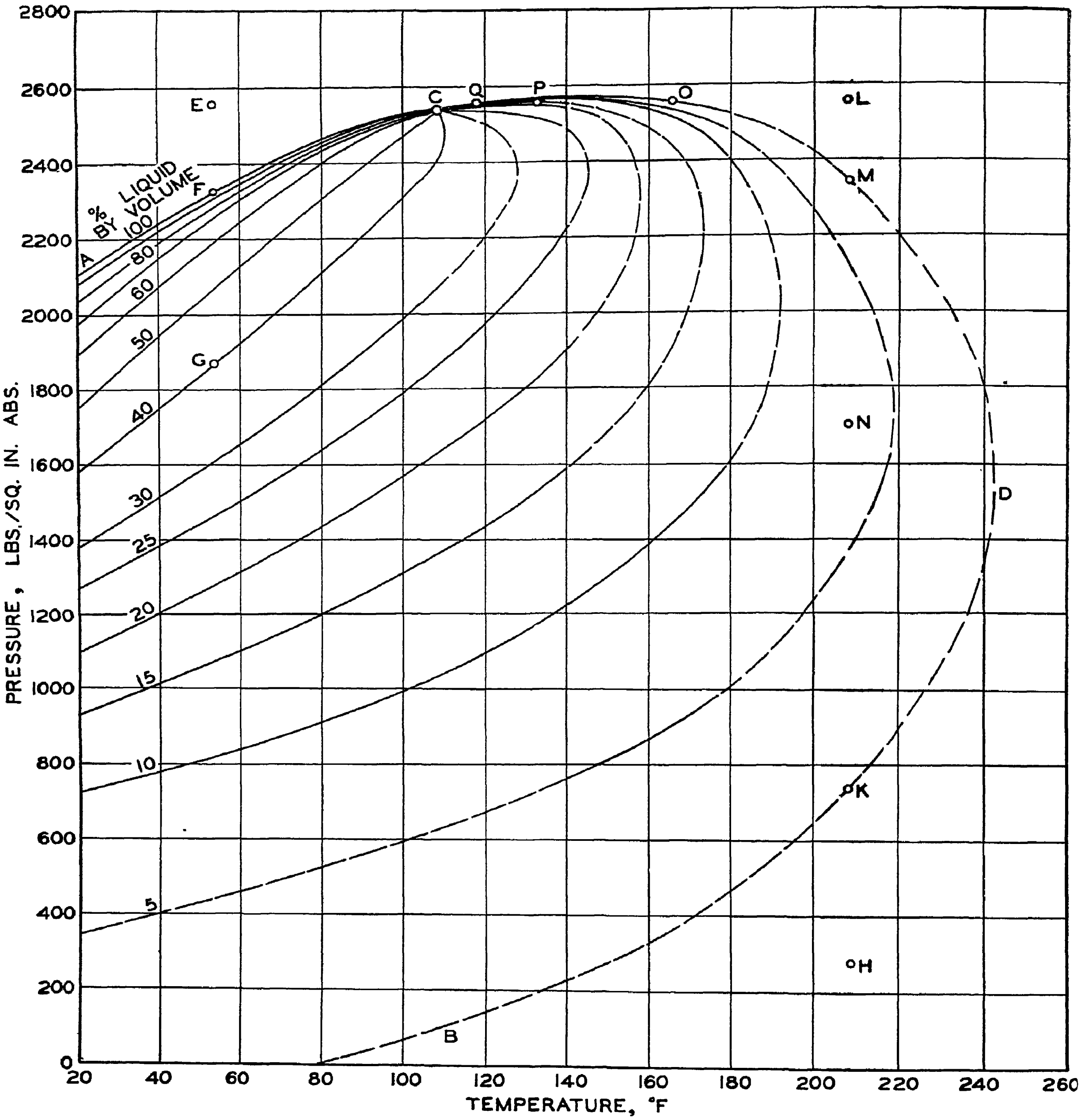


FIG. 8. Equilibrium constants at 2,200 P.S.I. and 101° F as a function of normal boiling-points.

TABLE II

Calculation of Phase Compositions and Gallons per Minute Content in Natural Gas-condensate Separator

Given the following field test data and analyses. Conditions of separator = 2,200 lb. per sq. in. and 101° F.

	Mol. fr. in vapour	*Mol. fr. in liquid*	*Mol. fr. in composite*	K_{exp}
Carbon dioxide	0·0041	..	0·0040	..
Methane	0·9276	0·3406	0·9159	2·720
Ethane	0·0303	0·0415	0·0305	0·730
Propane	0·0136	0·0297	0·0139	0·458
Isobutane	0·0042	0·0152	0·0044	0·278
n-Butane	0·0038	0·0167	0·0041	0·228
Isopentane	0·0023	0·0142	0·0025	0·162
n-Pentane	0·0016	0·0132	0·0018	0·121
Hexanes	0·0026	0·0463	0·0035	0·0561
Heptanes and heavier	0·0099	0·4826	0·0194	0·0205
	1·0000	1·0000	1·0000	..

Mol. wt. of heptanes and heavier in liquid = 159·5,
Sp. gr. of heptanes and heavier = 0·7994,

$$V=\sum\frac{Kz}{\frac{L}{V}+K},$$

where V = mols of vapour per mol well effluent,
L = mols of liquid per mol well effluent,
K = equilibrium constant at separator conditions,
z = mol fraction of component in well effluent.

To solve this equation values of V are assumed and the right-hand member of the equation is computed for each component. The cerrect value of V is that which equals the sum of the right-hand member of the equation for all components. Only the final value of V is given here.

Component	*Mol. fr. in well effluent, z*	*Equil. const. K (Fig. 8)*	*Kz*	$\frac{L}{V}+K$	*Vapour*		*Liquid*	
					$\frac{Kz}{\frac{L}{V}+K}$	*Mol. fr.*	*Mols per mol well effluent*	*Mol. fr.*
Carbon dioxide	0·0040	1·38	0·00551	1·3999	0·00395	0·00402	0·00005	0·00256
Methane	0·9159	2·50	2·293	2·5199	0·9100	0·9280	0·0059	0·3021
Ethane	0·0305	0·800	0·0244	0·8199	0·0298	0·0305	0·0007	0·03585
Propane	0·0139	0·445	0·00619	0·4649	0·0133	0·01358	0·0006	0·0307
Isobutane	0·0044	0·270	0·00119	0·2899	0·0041	0·00419	0·0003	0·01536
n-Butane	0·0041	0·222	0·00091	0·2419	0·00376	0·00384	0·00034	0·0174
Isopentane	0·0025	0·140	0·00035	0·1599	0·00219	0·00223	0·00031	0·01588
n-Pentane	0·0018	0·121	0·000218	0·1409	0·00155	0·00158	0·00025	0·0128
Hexanes	0·0035	0·079	0·000276	0·0989	0·00279	0·00284	0·00071	0·03635
Heptanes and heavier	0·0194	0·0173	0·000336	0·0372	0·00904	0·00922	0·01036	0·5310
	..	..	..	..	0·98048	1·00000	0·01952	1·00000

V assumed = 0·9805.

Density of liquid at 101° F. 2,200 lb. per sq. in. calculated as 0·686 g./c.c.
Mol. wt. of liquid calculated as 99·2.
Liquid content in gal. per min.:

$$\frac{1{,}000\times 0{\cdot}0195\times 99{\cdot}2}{379{\cdot}9805\times 8{\cdot}33\times 0{\cdot}686}=0{\cdot}91\text{ gallons per 1,000 cu. ft. gas.}$$

Experimental yield = 0·95 gal. per min.

REFERENCES

1. ANONYMOUS. *Oil and Gas J.* **43**, no. 45, 65 (17 Mar. 1945).
2. BUCKLEY and LIGHTFOOT. *A.I.M.E. Trans.* **142**, 232 (1941).
3. EILERTS *et al.* *A.G.A. Monthly*, **26**, 148 (1944).
4. HADDEN, S. T. Paper presented at A.I.Ch.E. meeting, Atlantic City (1946).
5. HANSON and BROWN. *Ind. Eng. Chem.* **37**, 821 (1945).
6. HANSON, RZASA, and BROWN. *Ind. Eng. Chem.* **37**, 1216 (1945).
7. KATZ, D. L. *A.I.M.E. Trans.* **127**, 159 (1938).
8. KATZ and HACHMUTH. *Ind. Eng. Chem.* **29**, 1072 (1937).
9. KATZ and KURATA. *Ind. Eng. Chem.* **32**, 817 (1940).
10. KATZ and RZASA. *Bibliography for Physical Behavior of Hydrocarbons Under Pressure and Related Phenomena*, 306 pp., Edwards Bros. Inc., Ann Arbor (1946).
11. KURATA and KATZ. *A.I.Ch.E. Trans.* **38**, 995 (1942).
12. LEWIS, J. O. *A.I.M.E. Trans.*, T.P. no. 2053 (July 1946).
13. NOBLE, F. G. *A.P.I. Drill. and Prod. Pract.*, p. 43 (1943).
14. OLDS, SAGE, and LACEY. *A.I.M.E. Trans.* **160**, 77 (1945).
15. ROLAND, C. H. *Ind. Eng. Chem.* **37**, 930 (1945).
16. ROLAND, SMITH, and KAVELER. *Oil and Gas J.* **39**, no. 46, 128 (27 Mar. 1941).
17. SAGE and LACEY. *A.P.I. Drill. and Prod. Pract.*, p. 308 (1941).
18. SAGE, HICKS, and LACEY. *Ind. Eng. Chem.* **32**, 1085 (1940).
19. SMITH and WATSON. *Ind. Eng. Chem.* **29**, 1408 (1937).
20. SOUDERS, SELHEIMER, and BROWN. *Ind. Eng. Chem* **24**, 517 (1932).
21. STANDING and KATZ. *A.I.M.E. Trans.* **155**, 232 (1944).
22. SUE and MILLER. *A.P.I. Drill. and Prod. Pract.*, p. 117 (1945).
23. THORNTON, O. F. *Oil and Gas J.* **45**, no. 28, 189 (16 Nov. 1946).
24. WEBBER, C. E. *A.I.M.E. Trans.* **142**, 192 (1941).

SELECTED BIBLIOGRAPHY

Bearce, H. W., and Peffer, E. L. *Density and Thermal Expansion of American Petroleum Oils.* U.S. Nat. Bur. Stand. Tech. Paper 77 (1916).

California Natural Gasoline Association, Bulletin, No. TS-441 (1945).

Cragoe, C. S., and Hill, E. E. *Bureau of Standards,* Dec. 1931, 'Thermal Expansion of Gasolines from 0/30°'.

Inst. Pet. J., 27, Nov. 1941, 'Expansion of Crude Petroleum, Petroleum Products and Allied Substances'.

Inst. Pet. J., July 1945, 'Tables for Measurement of Oil'.

Jessup, R. S. *Bureau of Standards,* Nov. 1930, 'Compressibility and Thermal Expansion of Petroleum Oils in the Range 0/300° C.'.

Measurement of Oil in Bulk, Part 1, Standard Weights and Measures. Inst. of Petroleum, London, 1932.

Natural Gasoline Association of America. *Ind. Eng. Chem.* **34,** 1240–5 (1942).

Natural Gasoline Association of America, Standard 2142 (Dec. 1942). *Standard Factors for Volume Correction and Specific Gravity Conversion of Liquefied Petroleum Gases and Volatile Gasolines.*

U.S. National Bureau of Standards as Circular C140, *National Standard Petroleum Tables* (1936).

U.S. National Bureau of Standards as Supplement to N.B.S. Circular C410, April 1937, *Abridged Volume Correction Table for Petroleum Oils.*

U.S. Bureau of Standards, Letter Circular LC-736, *Liquid Densities of Eleven Hydrocarbons found in Commercial C_4 Mixtures,* by C. S. Cragoe (Nov. 1943).

U.S. Bureau of Standards, Letter Circular LC-757, *Volume Correction Factors for C_4 Hydrocarbon Mixtures,* by C. S. Cragoe (July 1944).

INDEX OF NAMES

Abakumowsky, L. N., 112.
Adams, E., 97.
Adams, N. G., 9, 20, 77.
Adkins, H., 106, 112.
Alden, R. C., 77, 83.
American Petroleum Institute, 153.
Anderson, H. C., 78, 83.
Ando, S. J., 87, 88.
Anzilotti, W. F., 97.
Archer, S., 97, 113.
Archibald, A. C., 81, 83.
Armistead, G., 81, 83.
Armstrong, R. T., 103, 112.
Aschan, C. O., 58.
Ashford, T. A., 112.
Asinger, F., 79, 82, 83.
Atanasin, I. A., 89, 97.
Avanesov, D., 89, 97.
Ayling, E. E., 92, 97.

Backer, H. I., 71, 77.
Baird, W., 83.
Balandin, A. A., 81, 83, 86, 88.
Ball, J. S., 19, 20.
Barney, A. L., 112.
Bartlett, P. D., 82, 83.
Baryshnikova, A. N., 89, 97.
Bashulin, P. A., 88.
Bates, J. R., 62, 77.
Bearce, H. W., 192.
Beckett, C. W., 176, 180, 181.
Beckham, L. J., 112.
Beilstein, F. K., 58.
Bell, A. H., 20.
Berchelmann, W., 97.
Berg, L., 108, 112.
Berkman, G., 88.
Berkmann, M. G., 83.
Bernhauer, K., 96, 97.
Besley, D. M., 82, 83.
Bestougeff, N. A., 69, 77.
Bibb, C. H., 95, 97.
Billen, G. N., 113.
Binapfl, J., 94, 97.
Birch, S. F., 34, 82, 83.
Bishop, J. W., 81, 82, 83.
Blade, O. C., 20, 69, 77.
Blanc, G., 92, 97.
Block, H. S., 83, 112.
Block, L. D., 79, 83.
Bludworth, J. E., 83.
Bode, E., 85, 88.
Bolle, J., 97.
Bond, G. R., 104, 112.
Bone, W. A., 94, 105.
Bonnell, W. S., 82, 83.
Borchers, H., 92, 97.
Boultbee, A. H., 77.
Bowden, E., 95, 96, 97.
Boyd, T., 83.
Brain, G., 112.
Branch, G. E. K., 125.
Branner, G. C., 20.
Brooks, H. B., 150.
Brown, G. G., 187, 191.
Brown, H. C., 79, 83, 87, 88, 91, 97, 125.
Brown, M. L., 112.
Brown, R. A., 62, 77.
Bruun, J. H., 150.
Buchler, C. C., 70, 77.
Buckly, S. E., 191.
Bullock, J. L., 89, 97.
Burgoyne, J. H., 86, 88, 94, 97.
Burk, R. E., 83.
Butz, L., 112.
Byrnes, A. C., 98, 112.

Caesar, P. O., 95, 97.
Cahill, J. C., 152.
Calcott, W. S., 99, 112.
California Natural Gasoline Association, 192.
Calin, J., 97.
Calingaert, G., 151.
Callahan, J. R., 77.
Calvin, M., 125.
Campbell, D. S., 41.
Canant, F. C., 39, 41.
Cantuniari, I. D., 83.
Carbide and Chemicals Corporation, 109.
Carlson, G. H., 103, 104, 112.
Carmack, M., 90, 97.
Carpenter, J. A., 70, 77.
Carson, S. C., 82, 83.
Cauley, S. R., 39, 41.
Cavanaugh, R. M., 86, 88.
Chao, T. H., 125.
Chavanne, G., 85, 86, 88.
Cheyney, H. A., 83.
Chiurdoglu, G., 85, 88.
Chowdhury, J. K., 86, 88.
Church, J. M., 106, 112.
Churchill, J. W., 83.
Clark, G. C., 80, 83.
Clark, G. L., 71, 77.
Clarke, F. H., 83.
Condon, F. E., 82, 83.
Conn, J. B., 78, 83.
Cornet, Mlle, 88.
Corson, B. B., 97.
Cosby, J. N., 71, 77.
Coull, J., 107, 112.
Cowles, M. C., 70, 77.
Crafts, J. M., 97.
Cragoe, C. S., 192.
Craig, D., 110, 112.
Craven, E. C., 102, 112.
Crawford, J. G., 19, 20.
Criegee, R., 106, 112.
Cunneen, J. I., 100, 112.
Cutter, H. B., 91, 97.

Danzig, M. H., 83.
Davis, 66.
Davis, L. L., 37, 41.
Dean, E. W., 20.
Degering, E. F., 79, 83.
De Golyer, E., 42, 43.
De Golyer Mission, 30, 34.
Delgass, E. B., 39, 41.
Demann, W., 92, 97.
Demjanov, N. Ya, 103, 112.
Dermer, O. C., 101, 112.
Doak, K. W., 103, 112.
Docksey, P., 34, 41.
Doumani, T. F., 89, 97, 98, 112.
Dove, J. H., 34.
Dunphy, R. A., 83.
Dupont, P., 86, 88.
Dysinger, G. A., 101, 112.

Eberneder, F., 82, 83.
Eccleston, B. H., 20.
Edlund, K. R., 98, 99, 112.
Egloff, G., 41, 71, 77, 80, 81, 82, 83, 107, 108, 112.
Eichner, C., 83.
Eilerts, C. K., 191.
Elder, A. L., 109, 112.
Ellis, C., 98, 112.
Erhardt, O., 112.
Evans, D. B., 113.
Evans, T. W., 98, 99, 112.
Eyring, H., 78, 83.

Farmer, E. H., 85, 88, 98, 106, 109, 112.
Fawcett, E. W. M., 83.
Fehrer, H., 84.
Fenske, M. R., 77.
Ferris, S. W., 70, 71, 77.
Fischer, H. C. M., 77.
Flanagan, H. F., 152.
Flygan, H., 112.
Forster, M. O., 104, 113.
Forziati, A. F., 57, 58, 77, 152.
Francis, F. H., 70, 77.
Franke, N. W., 83.
Frantz, R. K., 97.
Freeth, F. A., 112.
Frey, F. E., 62, 77, 82, 83, 99, 102, 112.
Freytag, A., 83.
Friedel, C., 97.
Friedman, R. S., 99, 100, 112.
Friedmann, W., 80, 83.
Frolich, P. K., 80, 84, 109, 112.
Fuller, E. W., 97.
Fuson, R. C., 92, 97.

Gaboriault, A. L., 152.
Garton, E. L., 20, 41, 74, 77.
Gattermann, L. A., 92, 97.
Gekler, R. D., 81, 83.
Gilman, H., 96, 97.
Ginsburg, A., 92, 97.
Glasebrook, A. L., 81, 83, 86, 88.
Glasgow, A. R., 62, 77, 151, 152.
Glasstone, S., 78, 83.
Glushnev, N. F., 97.
Goldsby, A. R., 107, 112.
Gooding, R. M., 9, 20, 59, 77.
Granger, R., 85, 88.
Grassi-Cristaldi, G., 91, 97.
Graves, C. D., 70, 77.
Greensfelder, B. S., 81, 83.
Groll, H. P. A., 79, 83.
Grosse, A. V., 63, 77, 82, 83, 86, 88, 96, 97.
Grummitt, O., 81, 83.
Gurwitch, L., 69, 77.
Guthrie, B., 9, 20.
Guthrie, W. A., 34.

Hackmuth, K. H., 187, 189, 191.
Haddad, G. J., 103, 113.
Hadden, S. T., 191.
Haensel, V., 82, 83.
Hammett, L. P., 119, 124, 125.
Hansburg, M., 41.
Hansford, R. C., 80, 83.
Hanson, G. H., 187, 191.
Hardy, D. V. N., 105, 112.
Harman, R. A., 94, 97.
Harris, C. D., 105, 112.
Hart, H., 95, 97.
Hartig, M. J., 102, 112.
Hass, H. B., 78, 79, 83.
Hatch, L. F., 83.
Hauser, C. R., 125.
Hay, R. G., 107, 112.
Hearne, G., 79, 83.
Heinze, R., 41.
Heldman, J. D., 83.
Henderson, L. M., 70, 77.
Hendrickson, L., 73, 77.
Henline, P. W., 20.
Henne, A. L., 79, 83.
Hennion, G. F., 97.
Henriques, H. J., 72, 77.
Hepp, H. T., 77, 82, 83, 99.
Hered, W., 79, 83, 88.
Herington, E. F. G., 81, 83.
Heuer, W. W., 66, 77, 151.
Hey, D. H., 92, 97, 117.
Hickinbottom, W. J., 105, 112.
Hicks, B. L., 184, 191.
Hicks, M. M., 150.
Hicks-Bruun, M. M., 150.
Hill, E. E., 192.
Hinkel, L. E., 92, 97.
Hodge, E. B., 83.
Hofeditz, W., 125.
Hoffmann, K. A., 112.
Holde, D., 72, 77.
Holden, M. E. I., 112.
Holloway, C., 82, 83.
Holloway, J. H., 92, 97.
Holroyd, R., 83.
Hoog, H., 81, 83.
Hopff, H., 82, 83.
Horn, E., 125.
Houghton, W. F., 41.
Howe, A. P., 83.
Hufferd, R. W., 63, 77.
Hugel, G., 112.

Hughes, E. C., 102, 112.
Hughes, E. D., 125.
Hulla, G., 81, 82, 83, 108, 112.
Hurd, C. D., 107, 112.
Hutcheon, A. T., 73, 77.

Ingold, C. K., 89, 97.
Institute of Petroleum, 192.
Ipatieff, V. N., 82, 83, 87, 88, 96, 97, 99, 100, 102, 107, 111, 112.
Isacescu, D. A., 83, 97.

Jackson, E. A., 41.
Jackson, J. S., 41.
James, J. R., 95, 97.
Jenkins, G. I., 83.
Jensen, E. V., 101, 112.
Jessup, R. S., 192.
Johnson, W. H., 180.
Johnston, F., 125.
Jones, J. M., 37, 41.
Jones, S. O., 100, 112.
Joshel, L., 112.

Kabeler, H. H., 187, 189, 191.
Kamusher, M. D., 83.
Kane, S. S., 125.
Karasch, M. S., 79, 83, 85, 88, 91, 93, 97, 100, 101, 108, 109, 112, 116, 125.
Kasper, C., 150.
Kassel, L. S., 83.
Katz, D. L., 187, 191.
Katzenstein, Mlle, 88.
Kaveler, H. H., 187, 189, 191.
Kazanskii, B. A., 86, 88, 91, 97.
Kellerman, H., 83.
Kellogg, C. M., 19, 20.
Kelly, R. N., 108, 112.
Kern, J. G., 83.
Kewley, J., 41.
Kiefer, J. M., 113.
Kilpatrick, J. E., 83, 158, 163, 166, 176, 180, 181.
Kirkpatrick, S. D., 79, 83.
Kistiakowsky, G. B., 78, 83, 107, 112.
Kobe, K. A., 89, 93, 97.
Kobyls'kaya, M. V., 83.
Koch, J. A., 92, 97.
Kock, H., 81, 83.
Kolvoort, E. C. H., 71, 77.
Komarewsky, V. I., 77, 80, 81, 83, 112.
Kondakow, J. T., 98, 112.
Kostin, F. L., 88.
Kotelkov, N. Z., 86, 88.
Kraemer, A. J., 9, 17, 18, 19, 20.
Kraft, F., 70, 77.
Kranz, H., 63, 77.
Krapivin, S., 98, 112.
Krase, N W.. 92, 97.
Krassilchick, A., 101, 112.
Krebs, E., 92, 97.
Krey, W. ,97.
Kritschevski, J., 109, 112.
Kurata, F., 191.
Kurtz, S. S., 24, 67, 77.
Kvetinskas, B., 83.

Lacey, W. N., 184, 191.
Laidler, K. J., 78, 83.
Lane, E. C., 16, 19, 20, 41, 74, 77.
Lankelma, H. P., 83.
Lanning, M. J., 80, 83.
Lapworth, A., 97.
Larson, R. M., 19, 20.
Lawrence, C. D., 112.
Lawrosky, S., 77.
Lebedev, S. V., 109, 112.
Legatski, M. R., 77.
Legatski, T. W., 77.
Leighton, P. D., 83.
Leslie, R. T., 66, 77, 150, 151.
Letsinger, R. L., 112.
Levy, N., 103, 104, 112.
Lewis, G. N., 114, 118, 125, 153.
Lewis, J. O., 191.
Liddel, U., 150.
Lightfoot, J. H., 191.
Lipkin, M. R., 67, 77.
Little, E. L., 97.
Little, J. R., 103, 112.
Lock, G., 92, 97.
Loder, D. J., 86, 88.
Logan, L. J., 34.
Lovell, W. G., 81, 83, 86, 88.
Lueth, P. F., 97.

Mabery, C. F., 58, 70, 77.
MacPherson, G. R., 40, 41.
McAllister, E. N., 66.
McAteer, J. H., 83.
McBay, H. C., 97.
McBee, E. T., 83.
McCleary, R. F., 79, 83.
McCubbin, R. J., 106, 112.
McKeever, C. H., 92, 97.
McKenna, J. F., 96, 97.
McKittrick, D. C., 72, 77.
McReinolds, L. A., 77.
Magat, E. E., 112.
Mair, B. J., 63, 65, 66, 73, 77, 150, 151, 152.
Malkemus, J. D., 113.
Mansfield, J. V., 125.
Marder, M., 41.
Marek, L. F., 80, 83.
Markovnikoff, V., 58, 100, 112.
Marushkin, M. M., 83.
Maselli, C., 91, 97.
Matthews, M. A., 83.
Mattox, W. J., 81, 83, 88.
Matuczak, M. P., 77.
Mavity, J. M., 63, 77, 97.
May, E. M., 100, 112.
May, W. G., 73, 77.
Mayberry, M. G., 103, 112.
Mayes, H. A., 96, 97.
Mayo, F. R., 79, 83, 88, 100, 108, 109, 112, 125.
Meals, R. N., 96, 97.
Meier, H. H., 86, 88.
Melpoder, F. W., 77.
Merrell, J. C., 112.
Merrill, D. R., 9, 20.
Meyer, H., 96, 97.
Michael, A., 103, 104, 112.
Mikeska, L. A., 66, 77.
Milas, N. A., 94, 97, 106, 112.
Miller, E., 80, 84.
Miller, J., 191.
Miller, O., 88.
Mills, I. W., 77.
Minchin, S. T., 36, 41.
Miners, K. A., 73, 77.
Mitchell, E. T., 89, 97.
Mitchell, S., 82, 83.
Mithoff, R. C., 40, 41.
Moldavskii, B. L., 81, 83.
Moldner, R., 104, 112.
Montgomery, C. W., 83, 107, 108, 112.
Morgan, W. H., 92, 97.
Morrell, C. E., 109, 112.
Morton, A. A., 93, 97, 108, 112.
Moser, F. R., 71, 77.
Mousseron, M., 85, 88.
Moyer, W. W., 94, 97.
Mueller, E. F., 180.
Müller, J., 65, 72, 77.
Murphy, E. T., 152.
Murphy, G. B., 41.
Murphy, W., 9, 19, 20.
Murray, R. L., 83.

Nagle, W. M., 86, 88.
Nakatsuchi, A., 95, 97.
Nametkin, S. T., 72, 77, 102, 112.
Natelson, S., 99, 112.
Natural Gasoline Association of America, 192.
Naylor, R. F., 101, 112.
Nebylova, E., 83.
Neilson, C. A., 37, 41.
Nelson, E. F., 35, 41.
Nenitzescu, C. D., 83, 97.
Neumann, L. M., 16, 20.
Newitt, D. M., 80, 83, 88, 94, 97.
Nickels, J. E., 77.
Niedzielski, E. L., 92, 97.
Nifontova, S. S., 72, 77.
Nightingale, D., 95, 97.
Nikolaeva, A. F., 86, 88.
Noble, F. G., 191.
Nord, F. F., 92, 97.
Norris, J. F., 96, 97.
Norton, J. A., 110, 112.
Nozokina, T., 83.
Nysewander, C. W., 81, 83.

Obberright, E. A., 112.
Oberfell, G. G., 77.
O'Connor, M. J., 95, 97.
O'Kelly, A. A., 77, 82, 83.
Olds, R. H., 191.
Olson, L. E., 113.
Ormandy, W. R., 102, 112.

Padgett, A. R., 57, 77.
Pahlavonni, Mlle, 88.
Palmer, R. C., 95, 97.
Paneth, F., 125.
Parks, W. G., 94, 97.
Passino, H. J., 97.
Peffer, E. L., 192.
Perrin, M., 83.
Peters, W. A., 41.
Phillips, N. E., 81, 83.
Pignocco, J. M., 152, 180.
Pilat, S., 65, 72, 77.
Pines, H., 81, 83, 87, 88, 97, 99, 100, 102, 107, 112.
Pitkethly, R. C., 81, 83.
Pitz, H., 112.
Pitzer, K. S., 83, 153, 158, 163, 166, 172, 176, 180, 181.
Planckh, R., 72, 77.
Pogacnick, M., 71, 77.
Polanyi, M., 125.
Polly, O. L., 80, 83.
Powell, T. M., 83.
Prettre, M., 80, 83.
Price, C. C., 97, 117, 125.
Prosen, E. J., 83, 158, 163, 172, 176, 180.

Rall, H. T., 9, 20, 77.
Randall, D. I., 97.
Randall, M., 153.
Rappoport, P. L., 88.
Rasmussen, H. C., 80, 83.
Raymond, C. L., 83.
Read, A. T., 88, 97.
Reed, C. F., 83.
Rees, D. W., 20.
Reid, E. E., 100, 112.
Reid, F. B., 83.
Reistle, C. E., 69, 77.
Renoll, M. W., 79, 83.
Reppe, H., 109.
Rice, F. O., 125.
Richardson, R. E., 83.
Richter, H., 81, 83.
Rideal, E. K., 80, 81, 83, 84.
Riebsomer, J. L., 112.
Ries, H. E., 113.
Riesz, C. H., 77, 80, 83.
Riley, E. F., 79, 83.
Robb, J. A., 41.
Rodden, C. J., 99, 112.
Roduta, F. L., 94, 97.
Roland, C. H., 187, 189, 191.
Rose, F. W., 77, 150, 151.
Rossini, F. D., 58, 66, 67, 77, 78, 81, 83, 150, 151, 152, 158, 163, 166, 172, 176, 180, 181.
Rothrock, H. S., 125.
Rothstein, E., 97.
Rubinstein, D., 97.
Rueggeberg, W. H., 93, 97.
Rust, F. F., 79, 83, 86, 88, 100, 101, 112.
Rzasa, M. J., 191.

Saboor, M. A., 86, 88.
Sachanen, A. N., 69, 70, 71, 72, 75, 77, 80, 82, 83, 95, 97.
Sage, B. H., 184, 191.
Scaife, C. W., 103, 112.
Scanlan, J. T., 113.
Schaad, R. E., 107, 112.
Scheumann, W. W., 41.
Schicktanz, S. T., 73, 77, 150, 151.
Schmerling, L., 81, 82, 83, 97.
Schmidt, J., 103, 112.
Schneider, A., 82, 83.
Schneider, O., 112.

Schuit, C. A., 81, 83.
Schunemann, K. H., 72, 77.
Scott, W. D., 112.
Sedlak, V. A., 152.
Selheimer, C. W., 191.
Senseman, C. E., 94, 95, 97.
Sergienko, S. R., 88.
Seyler, R. C., 108, 112.
Shand, W. C., 81, 83.
Shell Development Co., 83.
Sherveda, L. G., 71, 72, 77.
Sidel Kovskaya, F. P., 88.
Sidorova, N. V., 96, 97.
Simmons, M. C., 9, 20.
Simons, J. H., 79, 83, 90, 94, 95, 96, 97.
Sipos, F., 40, 41.
Smirnova, N. V., 97.
Smith, A. E. W., 104, 112.
Smith, E. A., 78, 83.
Smith, H. M., 20, 41.
Smith, H. S., 77.
Smith, J. C., 100, 112.
Smith, L. I., 91, 97.
Smith, M. A., 71, 77.
Smith, M. A. C., 20, 74, 77.
Smith, R. A., 112.
Smith, R. K., 78, 82, 83, 84.
Smith, R. L., 191.
Smith, R. V., 187, 189, 191.
Smith, W. R., 107, 112.
Snow, R. D., 77, 102, 112.
Solovova, O. P., 88.
Soroos, H., 151.
Souders, M., 191.
Soule, L. F., 152.
Sowa, F. J., 97.
Spaght, E. M., 107, 112.
Spencer, C. C., 112.
Spengler, G., 104, 112.
Spinks, A. W., 150.
Spinks, J. W. T., 73, 77.
Spitzer, R., 181.
Standing, M. B., 187, 191.
Stanfield, K. E., 19, 20.
Staudinger, H., 117.
Stauff, J. Z., 83.
Steiner, H., 81, 83.
Stephens, H. N., 94, 97.
Stewart, J. F., 41.
Strating, L., 71, 77.
Streiff, A. J., 63, 66, 77, 151, 152.
Strong, W. O., 97.
Stubbs, J. J., 95, 97.
Sturgis, B. M., 96, 97.
Style, D. W. G., 125.
Sudborough, J. A., 104, 112.
Sudhoff, R. W., 83.
Sue, J. O., 191.
Suida, H., 72, 77.
Summer, G. L., 108, 112.
Sundralingham, A., 106, 112.
Sussman, S., 106, 112.
Suter, C. M., 103, 113.
Sutherland, L. M., 71, 77.
Swearingen, J. E., 81, 83.
Swern, D., 106, 113.
Symer, H. J., 112.

Tang, T. L., 88, 97.
Tannich, R. E., 57, 77.
Taylor, H. S., 78, 81, 84.
Taylor, M. D., 98, 112.
Taylor, R. C., 77.
Taylor, W. J., 152, 158, 172, 180.
Teller, E., 125.
Teter, J. N., 113.
Thacker, C. M., 80, 84.
Thomas, B. W., 57, 77.
Thomas, C. A., 84.
Thomas, C. L., 112, 113.
Thomas, R. J., 90, 97.
Thorne, H. M., 9, 19, 20.
Thornton, O. F., 191.
Thorpe, J. F., 85, 86, 98, 112.
Thorpe, R. S., 125.
Tilden, W. A., 104, 113.
Tilicheyev, M. D., 70, 77.
Tinker, J. M., 99, 112.
Titov, A. I., 79, 84, 89, 97.
Tongberg, C. O., 62, 77.
Townend, D. T. A., 84.
Truffault, R., 95, 97.
Trusty, A. W., 41.
Tsukervanik, I. P., 97.
Turkevich, J., 78, 81, 82, 84.
Turner, E. E., 97.
Turner, S. D., 39, 41.
Turova-Pollak, M. B., 87, 88.
Twigg, G. H., 80, 84.
Tydeman, F. W. L., 19, 20.

Ubbelohde, A. R., 80, 84.
Universal Oil Products Co., 41.
Urry, W. H., 97, 101, 112.
U.S. National Bureau of Standards, 153, 192.

Vaala, G. T., 96, 97.
Van Arsdale, P. H., 82, 83.
Van Artsdalen, E. R., 78, 83.
Varteressian, K. A., 77.
Vaughan, W. E., 79, 83, 86, 88, 100, 101, 113.
Vavon, G., 92, 97.
Veatch, F., 102, 112.
Verheus, J., 81, 83.
Verver, C. G., 71, 77.
Virobianz, R. A., 75, 77.
Vsevolozhskaya, E. V., 88.
Vyatskin, I., 97.

Wackher, R. C., 83, 84.
Wade, G., 19, 20.
Wagman, D. D., 152, 158, 166, 172, 180.
Walker, J. C., 84.
Walker, J. F., 84.
Walling, C., 100, 112.
Wallington, W. R., 77.
Walsh, A. D., 80, 84.
Ward, C. C., 16, 20.
Ward, D., 97.
Washburn, E. W., 126, 150, 151.
Wassilieff, N. A., 71, 72, 77.
Waterman, H. I., 55, 66.
Waters, W. A., 84, 106, 113, 117.
Watkins, C. W., 77.
Watson, K. M., 35, 41, 191.
Weaver, W. J., 112.
Webber, C. E., 187, 191.
Weber, P., 83.
Weinmayr, V. J., 99, 112.
Weitzel, R., 113.
Wells, J. N., 111, 113.
Weltby, A. B., 77.
Werner, H. G., 176, 181.
West, I. R., 103, 113.
Westhaven, J. W., 152.
Westheimer, F. H., 90, 97.
Westlake, H. E., 103, 113.
Wheeler, R. V., 105.
White, J. D., 150, 151.
Whitlock, M. H., 103, 112.
Whitmore, F. C., 92, 97, 106, 112, 125.
Wiezewich, P. J., 80, 84.
Williams, M. G., 172, 180.
Willingham, C. B., 65, 66, 77, 151, 152, 180.
Willson, C. O., 34.
Wilson, E., 82, 83.
Wilson, P. J., 111, 113.
Wilson, R. E., 93, 97.
Wolff, H. I., 72, 77.
Wood, J. L., 113.
Wood, W. L., 83.

Yannaquis, N., 71, 73, 77.
Young, S., 58.
Young, W. S., 77.
Yula, R. W., 94, 97.

Zelinsky, N., 58, 85, 88.
Ziegler, K., 125.
Zook, H. D., 125.
Zorn, H., 107.
Zuidema, H. H., 80, 84.
Zuiderweg, F., 81, 83.

INDEX OF SUBJECTS

Abqaiq oilfield, 22, 32.
Abu Durba oilfield, 34.
Abu Hadriya oilfield, 22, 32.
Acetates, from olefines, 98.
Acetylenes:
  butadiene from, 109.
  equilibrium constants, 170.
  thermodynamic properties, 166.
  trimerization, equilibrium constants, 174.
Adipic acid, from cyclohexane, 86.
Alabama, crude oil, characteristics, 9.
Albania, crude oil production, 46.
Alcohols, alkylation, 96.
1-Alkene mono-olefines, cyclization, equilibrium constants, 177, 180.
1-Alkenes:
  equilibrium constants:
    dehydrogenation, 171.
    dimerization, 165, 166.
    hydrogenation, 165, 166.
  thermodynamic stability, 162.
Alkyl radicals, 166.
Alkylaromatics, sulphonation, 91.
Alkylate, composition, 62.
Alkylation:
  hydrogen fluoride, 99.
  paraffin, 82.
  reactions, 122.
  sulphuric acid, 99.
Alkylbenzenes:
  equilibrium concentrations, 173.
  hydrogenation, equilibrium constants, 177, 179.
  isomerization, free energy, 172.
  thermodynamic properties, 172.
  thermodynamic stability, 172.
Alkylcyclohexanes:
  equilibrium concentrations, 178, 179.
  isomerization, free energy, 177.
  thermodynamic properties, 176.
  thermodynamic stability, 177.
Alkylcyclopentanes:
  cyclization, equilibrium constants, 176.
  thermodynamic properties, 176.
  thermodynamic stability, 176.
Alkylsulphate detergents, 102.
Alkynes:
  thermodynamic stability, 168.
  trimerization, equilibrium constants, 175.
Allene, structure, 108.
Amylene, nitrosyl chloride addition, 104.
Aniline point, 36.
Anthracene, oxidation, 94.
A.P.I. mid-per cent. curve, 37, 38.
A.P.I. Research Project, 44, 184–5.
Arabia, *see* Saudi Arabia.
Argentine, crude oil production, 44, 45.
Arkansas, crude oil:
  aviation base stock data, 11.
  characterization, 9.
  production and reserves, 4.
Aromatics:
  aldehyde formation:
    Gattermann reaction, 92.
    Gattermann–Koch reaction, 92.
  alkyl:
    hydrogen atom reaction, 93.
    isomerization, 96.
    sulphonation, 91.
  alkylation, 95, 99.
  carbon monoxide reaction, 92.
  chemistry, 89–97.
  chloromethylation, 91.
  halogenation, 91.
  in gasoline, 58.
  Jacobsen reaction, 91.
  mercuration, 93.
  metalation, 93.
  nitration, 89.
  oxidation, 93.
  reduction, 91.
  sodium derivatives, 93.
  sulphonation, 90.
Asphalts, evaluation, 41.
Atoms, configurations, 114.
Austria, crude oil production, 44, 46.
Azeotropic mixtures, boiling-points, 128.

Bahrein Island:
  crude oil:
    production, 30, 44.
    products from, 28–9, 33.
  refineries, 30.
Belgium–Luxembourg, oil imports, 50.
Benzene:
  aldehydes from, 92.
  alkylation, 96.
    equilibrium constants, 172, 174.
    with butadiene, 111.
  characterization factor, 35.
  chloromethylation, 92.
  dinitrophenol from, 90.
  ethylation, 99.
  free energy of formation, 156.
  hydrogenation, 91.
  molecule, 89.
  nitration with nitrogen dioxide, 89.
  oxidation, 94.
  oxynitration, 89.
  phosgene reaction, 93.
  reduction, 91.
  sodium derivatives, 93.
Benzoic acid:
  preparation, 93.
  sulphuric acid reaction, 119.
Benzyl radicals, 116.
Bicyclic hydrocarbons, synthesis, 111.
Boiling-point, pressure changes, 127.
Boiling-point–gravity constant, 36.
British Borneo, crude oil production, 44, 45.
Buna S rubber, 111.
Burgan oilfield, 33.
Burma, crude oil production, 44, 45.
Butadiene:
  benzene alkylation, 111.
  bromination, 109.
  crotonaldehyde addition, 110.
  dibenzoylethylene addition, 111.
  hydrogen bromide reaction, 109.
  maleic anhydride reaction, 110.
  methylene malonic ester addition, 111.
  OXO reaction, 111.
  ozone reaction, 112.
  p-benzoquinone addition, 110.
  polymerization, 111.
  production, 108.
  structure, 108.
Butanes:
  catalytic reactions, 81.
  equilibrium concentrations, 161.
  equilibrium constants, 170.
  oxidation, cool flame, 80.
Butenes:
  carbon monoxide-steam reaction, 105.
  equilibrium concentrations, 164.
  equilibrium constants, 170.
  isomerization, 107.
    free energy, 163.
  nitrogen tetroxide reaction, 104.
  sulphuric reaction, 102.
Butylcyclopentane:
  hydrogenation, 86.
  oxidation, 86.
Butyles:
  equilibrium concentrations, 169.
  equilibrium constants, 170.
  isomerization, free energy, 168.

California, crude oil:
  aviation base stock data, 10.
  characteristics, 9.
  characterization factor, 36.
  production and reserves, 4.
  toluene and naphthene content, 13.
Canada, crude oil production, 44, 45.
Cannizzaro reaction, 123.
Carbon-hydrogen ratio, 36.
Carbonium ions:
  formation, 118.
  reactions, 119.
Ceresin, petroleum, 69.
Characterization factor of crude oil, 35.
Characterization gravity, 36.
China, crude oil production, 45.
Chlorination, peroxide effect, 91.
Chloroketones, from olefines, 98.
Chloromethylation, 92.
Colombia, crude oil production, 44, 45.
Colorado, crude oil:
  characteristics, 14.
  production and reserves, 5.
Correlation index, 36.
Cracking stocks, evaluation, 40.
Crude oil:
  A.P.I. mid-per cent. curve, 37.
  aromatic, 76.
  aromatic-asphalt, 76.
  asphaltic, 74, 76.
  A.S.T.M. end point, relation to true boiling-point, 38.
  aviation base stock data, 9.
  base of, 36.
  characterization factor, 35.
  classification, 36.
    chemical, 75.
    commercial, 74.
    geological identification, 73.

Crude oil (*cont.*)
  evaluation, 35–41.
  lubricant fraction, hydrocarbon separation, 139.
  naphthenic, 76.
  naphthenic-aromatic, 76.
  naphthenic-aromatic-asphaltic, 76.
  Oklahoma (Ponca), hydrocarbons in, 139.
  paraffinic, 74, 75.
  paraffinic-naphthenic, 76.
  property curves, 38.
  ring analysis, 75.
  salt content, 37.
  sulphur distribution, 37.
  toluene content, 60.
  viscosity-gravity constants, 36.
  wax content, 69.
  world production and reserves, 42.
Cumene, free energy of formation, 156.
Cyclic hydrocarbons, chemistry, 85.
Cycling, vapour-liquid equilibria, 182–92.
Cycloheptane, isomerization, 87.
Cyclohexane:
  adipic acid from, 86.
  alkylation, 87.
  bromination, 85.
  carboxylation, 87.
  chlorination, 85.
  combustion, 86.
  cyclohexanone from, 86.
  dehydrogenation, 86.
  hydrogenation, 86.
  isomerization, 86.
  sulphoxidation, 87.
  sulphuryl chloride reaction, 87.
Cyclohexanone, from cyclohexane, 86.
Cyclohexene:
  isopentanethiol reaction, 100.
  oxidation, 106.
  thioglycollic acid reaction, 100.
  thiophenol reaction, 100.
Cyclohexene dithiocyanate, 101.
Cyclopentadiene:
  bromination, 109.
  condensation with ethylene, 111.
  maleic anhydride reaction, 110.
  polymerization, 111.
  structure, 108.
Cyclopentane, cyclopentanone from, 86.
Cyclopentanone, from cyclopentane, 86.
Cylinder stock, evaluation, 41.
Cymene:
  nitration, 89.
  oxidation, 95.

Dammam oilfield, 22, 32.
Denmark, oil imports, 50.
Detergents:
  alkylsulphates, 102.
  Igepal, 102.
1, 2-Dialkylcyclopentanes, synthesis, 85.
Dialkylnaphthenes, structure, 85.
Diallyl, structure, 108.
Diesel fuel:
  diesel index, relation to other constants, 36.
  evaluation, 40.
Diesel index, 36.
Diisobutene:
  alkylation, 99.
  isomer determination, 106.
  ketones from, 98.
Diisopropyl:
  fuel performance, 78.
  nitration, 79.
Dimethylbenzene, free energy of formation, 156.
Dimethylbutadienes, bromination, 109.
2, 2-Dimethylbutane, fuel performance, 78.
2, 3-Dimethylbutane, fuel performance, 78.
Dimethylcyclohexanes, oxidation, 85.
1, 3-Dimethylcyclohexane, synthesis, 85.
1, 2-Dimethylcyclohexene, oxidation, 106.
Dimethylcyclopentane, oxidation, 85.
1, 2-Dimethylcyclopentane, isomerization, 87.
Diolefines:
  chemistry, 108.
  Diels–Alder condensation, 110.
  halogen reaction, 109.
  hydrogen bromide reaction, 109.
  hydrogen-carbon monoxide reaction, 111.
  hydrogen chloride reaction, 109.
  polymerization, 111.
  sulphur dioxide reaction, 110.
Distillates:
  cracked, characterization factor, 35.
  Pennsylvania, characterization factor, 35.
  Smackover, characterization factor, 35.
Distillation:
  azeotropic, 128.
  columns at Bureau of Standards, 127.
  extractive, 128.
  fractionation, 126.
Durene sulphuric acid, Jacobsen reaction, 91.

Ecuador, crude oil production, 44, 45.
Egypt:
  Abu Durba field, 34.
  crude oil:
    analyses, 34.
    products from, 34.
    production, 30, 34, 44, 45.
  Gemsah field, 34.
  Hurghada field, 34.
  Ras Gharib field, 34.
  refineries, 30.
  Sudr field, 34.
Eire, oil imports, 50.
Esters, from olefines, 98.
Ethane:
  catalytic reaction, 80.
  equilibrium constants, 170.
Ethanol, *see* Ethyl alcohol.
Ethyl alcohol:
  butadiene from, 109.
  dehydration, 121.
Ethyl alcohol-hydrocarbon mixtures, boiling-points, 128.
Ethyl benzene:
  free energy of formation, 156.
  hydrogen atom reaction, 93.
  oxidation, 94.
Ethylcyclopentane:
  hydrogenation, 86.
  oxidation, 86.
Ethylene:
  alkylation, 82.
    equilibrium constants, 167.
  ammonia reaction, 105.
  carbon monoxide-steam reaction, 105.
  catalytic reactions, 80.
  equilibrium constants, 170.
  isobutane reaction, 99.
  nitrogen tetroxide reaction, 104.
  oxidation, 105.
  polymers, 107.
  sodium bisulphite reaction, 100.
  sulphur reaction, 103.
  sulphuric acid reaction, 102.
  synthetic lubricants, 107.
Ethylene chlorhydrin, 101.
Ethylene dithiocyanate, 101.

Finland, oil imports, 50.
Fischer–Tropsch process, fluid catalytic, 80.
Florida, crude oils:
  characteristics, 14.
  production and reserves, 5.
France:
  crude oil production, 46.
  oil imports, 50.
Fuel oil, evaluation, 40, 41.

Gas oil:
  aromatic content, 63.
  characterization factor, 36.
  composition, 62.
  cracked residue, characterization factor, 35.
  hydrocarbons in, 63.
  ring analysis, 63.
  synthetic, composition, 63.
Gasoline:
  absorption, characterization factor, 35.
  alkylate, composition, 62.
  composition, 56–62.
  cracked, composition, 60.
  evaluation, 40.
  hydrocarbons in, 145.
  lead susceptibility, 40.
  natural:
    characterization factor, 35.
    composition, 56.
    hydrocarbons in, 57.
  polymer:
    composition, 62.
    ketones from, 98.
  Ponca City, hydrocarbons in, 58, 59.
  straight-run, composition, 57.
  synthetic, composition, 60.
Gattermann reaction, 92.
Gattermann–Koch reaction, 92.
Gemsah oilfield, 34.
Germany:
  crude oil production, 44, 46.
  oil imports, 50.
Great Britain:
  crude oil production, 46.
  oil consumption, 49.
  oil imports, 50.
  oil refining, 49.

Halogen acids, olefines reaction, 100.
Hemimellitene, free energy of formation, 156.
Heptane:
  catalytic reactions, 81.

Heptane (*cont.*)
  cyclization, equilibrium constants, 174.
  equilibrium concentrations, 162.
Hexadecane, oxidation, 80.
Hexahydromesitylene, isomerization, 87.
Hexanes:
  characterization factor, 35.
  cracked, isomers, 62.
  cyclization, equilibrium constants, 174.
  equilibrium concentrations, 162.
  fuel performance, 82.
  isomerization, 81.
  nitration, 79.
  nitrosyl chloride reaction, 82.
Hexenes:
  equilibrium concentrations, 166.
  free energy of isomerization, 164.
  isomerization, 107.
Hexylbromide, isomerization, 96.
Hostapon process, 82, 87.
Hungary, crude oil production, 44, 46.
Hurghada oilfield, 34.
Hydrocarbons:
  crystallization, 137.
  determination, 55.
  equilibrium constants, 158.
  fractionation, 126.
  free energy of reaction, 158.
  heat of reaction, 158.
  in gasoline fraction, 58, 59, 145.
  in lubricant fraction, 139.
  in naphtha, 14.
  in Oklahoma crude, 139.
  isolation, 126–52.
  petroleum, 55–7.
  purity determination, 137.
  ring analysis, 55.
  separation: 55
    by adsorption, 132.
    by distillation, 126.
    by extraction, 130.
    by fractionation, 126.
  thermodynamic properties, 153–81.
Hydrocarbons-absorber oil, equilibrium constants, 187.
Hydrocol process, 80.
Hydropolymerization, 102.

Igepal detergents, 102.
Illinois, crude oil:
  aviation base stock data, 11.
  characteristics, 14.
  production and reserves, 5.
  toluene and naphthene content, 13.
India, crude oil production, 44, 45.
Indiana, crude oil:
  characteristics, 14.
  production and reserves, 5.
Indonesia, crude oil production, 44.
Iran:
  crude oil:
    analyses, 31.
    production, 30, 44.
    products from, 31.
  natural gas, analysis, 30.
  refineries, 30.
Iraq:
  crude oil:
    analysis, 31.
    production, 30, 31, 44.
    products from, 32.
  refineries, 30.
Isoamylcyclopentane, hydrogenation, 86.
Isobutane:
  alyklation, 99.
  chlorsulphonation, 82.
  ethylene reaction, 99.
Isobutene:
  alkylation, 99.
    equilibrium constants, 167.
  amylsodium reaction, 108.
  condensation with methanol, 99.
  nitrogen tetroxide reaction, 104.
  polymerization product, 62.
  sodium bisulphite reaction, 100.
  sulphur dioxide reaction, 102.
  sulphuric acid reaction, 102.
Isobutyl alcohol, dehydration, 120.
Isobutylene, alkylation reaction, 122.
Isomerization, catalysts for, 81.
Isopentane:
  alkylation, 99.
  demethylation, 82.
Isoprene:
  hydrogen bromide reaction, 110.
  hydrogen chloride reaction, 110.
  maleic anhydride reaction, 110.
  polymerization, 111.
  sulphur dioxide reaction, 110.
Isoprene sulphone, 110.
Isopropylbenzene, free energy of formation, 156.
Italy, oil imports, 50.

Japan, crude oil production, 44, 45.

Kansas, crude oil:
  characteristics, 14.
  production and reserves, 5.
  toluene and naphthene content, 13.
Kekulé molecule, 89.
Kentucky, crude oil:
  characteristics, 14.
  production and reserves, 5.
Kerosine, evaluation, 40.
Ketones, from olefines, 98.
Kuwait:
  Burgan field, 33.
  crude oil:
    analyses, 33.
    production, 30, 33, 44.

Louisiana, crude oil:
  aviation base stock data, 11.
  characteristics, 14.
  production and reserves, 5–6.
  toluene and naphthene content, 13.
Lubricating oil:
  asphaltic-base, properties, 64.
  composition, 64.
  cyclic hydrocarbons, 66.
  fractionation, 65.
  hydrocarbon separation, 139.
  hydrocarbons in, 65.
  oxidation, 80.
  paraffin-base, properties, 64.
  paraffinic side chains in, 66.
  Pennsylvania, characterization factor, 35.
  ring structure, 64, 66.
  synthetic polymers, 107.
Mersols, 82.
Mesitylene, free energy of formation, 156.
Methane:
  carbon monoxide from, 80.
  nitration, 79.
  oxidation, 80.
  sulphur reactions, 80.
Methane-butane:
  equilibrium constants, 185.
  phase diagram, 184.
Methylacetylene, trimerization, equilibrium constants, 174.
Methylbenzene, free energy of formation, 156.
2-Methyl-2-butene, alkylation, equilibrium constants, 167.
2-Methylbutene-2, nitric acid addition, 104.
Methylcycloheptane, isomerization, 87.
Methylcyclohexane:
  alkylation, 87.
  bromination, 85.
  toluene from, 86.
Methylcyclohexene:
  isopentanethiol reaction, 100.
  thioglycollic acid reaction, 100.
  thiophenol reaction, 100.
1-Methylcyclohexene, oxidation, 106.
3 - Methylcyclohexene - 1 - dithiocyanate, 101.
Methylcyclopentane, hydrogenation, 86.
Methyl-*d*-heneicosyl-methane, 71.
Methylethylbenzenes, free energy of formation, 156.
1, 1-Methylisopropylethylene, alkylation, 122.
Mexico, crude oil production, 44, 45.
Michigan, crude oil:
  characteristics, 14.
  characterization factor, 36.
  production and reserves, 6.
Middle East:
  crude oils, 30–4.
  producing fields, 30.
  refineries, 30.
Mid-per cent. curve, 37, 38.
Mississippi, crude oil:
  characteristics, 14.
  production and reserves, 6.
Mixtures:
  binary, vapour-liquid equilibria, 184.
  complex, vapour-liquid equilibria, 185.
Mono-olefine hydrocarbons, chemical thermodynamic properties, 163.
Montana, crude oil:
  aviation base stock data, 11.
  characterization, 14.
  production and reserves, 6.
  toluene and naphthene content, 13.

Naphtha: cracked, characterization factor, 45.
  hydrocarbon content, 14.
Naphthalene:
  C_7, in U.S.A. crude oils, 13.
  oxidation, 94.
  sulphonation, 90.
Naphthenes:
  alkylation, 87.
  bromination, 85.
  carboxylation, 87.
  chemistry, 85–8.

Naphthenes (*cont.*)
  dehydrogenation, 86.
  halogenation, 85.
  hydrogenation, 86.
  in gasoline, 58.
  isomerization, 86.
  oxidation, 85.
  reaction with benzene, 96.
  sulphuryl chloride reaction, 87.
Natural gas, oxidation, cool flame, 80.
Natural gas–crude oil, equilibrium constants, 187.
Natural gas–distillate, equilibrium constants, 187.
Natural gas–natural gasoline, phase diagram, 183.
Natural gasoline, *see* Gasoline.
Nebraska, crude oil:
  characteristics, 14.
  production and reserves, 6.
Netherlands:
  crude oil production, 44, 46.
  oil imports, 50.
Netherlands East Indies, crude oil production, 44.
New Mexico, crude oil:
  aviation base stock data, 11.
  characteristics, 14.
  production and reserves, 6.
  toluene and naphthene content, 13.
Nitration of paraffins, 79.
n-Nonane, cyclization, equilibrium constants, 174.
Nonyl-di-heneicosyl-methane, 71.
Norway, oil imports, 50.

Octane:
  characterization factor, 35.
  cyclization, equilibrium constants, 174.
  equilibrium concentrations, 162.
  free energy of isomerization, 161.
Octene-1:
  acetic acid addition, 101.
  bromoform addition, 101.
  carbon tetrabromide addition, 101.
  carbon tetrachloride addition, 101.
  chloroform addition, 101.
  phosphorus trichloride addition, 101.
Oil industry, finance, 51–2.
Oklahoma, crude oil:
  aviation base stock data, 11.
  characteristics, 14.
  production and reserves, 6.
  toluene and naphthene content, 13.
Olefines:
  acetates from, 98.
  amines reaction, 105.
  ammonia reaction, 105.
  aromatics alkylation, 99.
  autoxidation, 106.
  carbon monoxide-steam reaction, 105.
  chemistry, 98–113.
  chlorination, 101.
  chloroketones from, 98.
  condensation:
    with acid anhydrides, 98.
    with acid chlorides, 98.
    with alcohols, 99.
    with organic acids, 98.
  cyclic, alkylation, 96.
  dioxane sulphotrioxide reaction, 103.
  disulphotrioxide reaction, 103.
  esters from, 98.
  glycols from, 106.
  halogen acids reaction, 100.
  halogen addition, 101.
  hydrogen sulphide reaction, 100.
  hydroxylation, 106.
  hypochlorous acid reaction, 101.
  isomerization, 107, 121.
  ketones from, 98.
  mercaptans reaction, 100.
  metal compounds, 108.
  metallation, 108.
  nitric acid addition, 104.
  nitrogen tetroxide reaction, 103.
  nitrosyl chloride addition, 104.
  oxidation, 105.
  palladium compounds, 108.
  paraffin alkylation, 99.
  phenols alkylation, 99.
  platinum compounds, 108.
  polyhalogenated compounds addition, 101.
  polymerization, 106.
  sodium bisulphite reaction, 100.
  sulphur dioxide reaction, 102.
  sulphur reaction, 103.
  sulphuric acid reaction, 102.
  synthetic lubricants, 107.
  thioacetic acid reaction, 100.
  thiocyanogen reaction, 101.
  thiophenol reaction, 100.
Organic reactions, mechanisms of, 114–25.
OXO synthesis, 105, 111.

Palestine, refineries, 30.
Palladium-olefine compounds, 108.
Parachor, 36.
Paraffins:
  aliphatic chemicals from, 78.
  alkylation, 82, 99.
  bromination, 79.
  characterization factor, 35.
  chemistry, 78–84.
  chlorination, 78.
  chlorsulphonation, 82.
  cyclization, equilibrium constants, 174, 175, 178.
  dehydrogenation, 80.
    equilibrium constants, 171.
  fluorine action, 79.
  halogenation, 78.
  in gasoline, 57.
  in lubricating oils, 65.
  in petroleum waxes, 69.
  isomerization, 81.
  nitration, 79.
  oxidation: 79.
    catalytic, 80.
    cool flame, 80.
    high temperature, 80.
    liquid phase, 80.
  physical properties, 78.
  reaction with aromatics, 96.
  sulphonation, 82.
  sulphur reactions, 80.
  sulphuryl chloride action, 79.
  thermodynamic stability, 157, 158.
Paraffin systems, quintary, equilibrium constants, 187.
Paraffin wax, *see* Wax, petroleum.
Parawax, 72.
Pennsylvania, crude oil:
  characteristics, 14.
  production and reserves, 7.
1, 3-Pentadiene, maleic anhydride reaction, 110.
Pentanes:
  equilibrium concentrations, 161.
  equilibrium constants, 170.
  isomerization, 81.
Pentaphenylcyclopentadienyl radical, 116.
Pentenes:
  amylsodium reaction, 108.
  equilibrium concentrations, 164.
  equilibrium constants, 170.
  free energy of isomerization, 163.
  isomerization, 107.
  sulphuric acid reaction, 102.
Pentynes:
  equilibrium constants, 170.
  isomerization, free energy, 170.
Peru, crude oil:
  characterization factor, 36.
  production, 44, 45.
Phenols, alkylation with olefines, 99.
Phosgene, reaction with benzene, 93.
Piperylene, *see* 1, 3-Pentadiene.
Platinum-olefine compounds, 108.
Poland, crude oil production, 44, 46.
Polyethylene, production, 107.
Polymer gasoline, composition, 62.
Polythene, production, 107.
Portugal, oil imports, 50.
Prices, oil, trends, 50.
Production, cycling, vapour-liquid equilibria, 182–92.
Propane:
  characterization factor, 35.
  equilibrium constants, 170.
  fluorination, 79.
  oxidation, cool flame, 80.
Propene:
  ammonia reaction, 105.
  carbon monoxide-steam reaction, 105.
  halogen acid reaction, 100.
  nitrogen tetroxide reaction, 104.
  sodium bisulphite reaction, 100.
Property curves, 38.
Propylbenzene, free energy of formation, 156.
Propylcyclopentane, hydrogenation, 86.
Propylene:
  alkylation, equilibrium constants, 167.
  chlorination, 79.
  equilibrium constants, 170.
Propyne, equilibrium constants, 170.
Pseudocumene, free energy of formation, 156.

Qatar, crude oil:
  analysis, 34.
  production, 30.
Qatif oilfield, 22, 32.

Range oil, evaluation, 40.
Ras Gharib oilfield, 34.
Reactions:
  acidic, 117.
  atomic and free radical, 115.
  basic, 122.
  Cannizzaro, 123.
  carbanion, 122.

Reactions (*cont.*)
  carbonium ion, 117.
  Gattermann, 92.
  Gattermann–Koch, 92.
  organic, mechanisms of, 114–25.
  polymerization, 116.
Reed chlorsulphonation of paraffins, 82.
Refining:
  charging stocks, evaluation, 38.
  economic trends, 46–7.
  operating data, 37.
  world capacity, 46–7.
Residuum, cracked, characterization factor, 35.
Rumania, crude oil production, 44, 45.

Sarawak, crude oil production, 45.
Saudi Arabia:
  Abqaiq field, 22, 32.
  Abu Hadriya field, 22, 32.
  crude oil:
    analyses, 23, 33.
    Dammam, products from, 33.
    lubricating oil production, 25–7.
    production, 30, 32, 44.
    products from, 22–7, 33.
  Dammam field, 22, 32.
  Qatif field, 22, 32.
  refineries, 30.
Smoke point, 36.
Soap acids, from paraffins, 80.
Solvents, evaluation, 40.
Styrene, aniline reaction, 105.
Styrene dithiocyanate, 101.
Sudr oilfield, 34.
Sulphonation, 90.
Sweden, oil imports, 50.
Switzerland, oil imports, 50.

Tetramethylethylene, nitrogen tetroxide reaction, 103.
Texas:
  crude oil:
    aviation base stock data, 12.
    characteristics, 17.
    production and reserves, 7.
    toluene and naphthene content, 13.
  East, crude oil, characterization factor, 36.
  Panhandle, crude oil, analysis, 19.
Thiocyanation, 101.
Toluene:
  aldehydes from, 92.
  alkylation, 96.
  chlorination, 91.
  chloromethylation, 92.
  free energy of formation, 156.
  from methylcyclohexane, 86.
  in crude oil, 60.
  in U.S.A. crude oils, 13.
  nitration, 89.
  oxidation, 94.
  reduction, 91.
  sodium derivatives, 93.
  sulphonation, 90.
Trimethylbenzenes, free energy of formation, 156.
Trimethylbenzoic acid, sulphuric acid reaction, 117.
Trimethylethylene:
  aniline reaction, 105.
  nitrogen tetroxide reaction, 103.
2,2,4-Trimethylpentane:
  catalytic reactions, 81.
  reaction with benzene, 96.
Trinidad, crude oil production, 44, 45.
Triphenylcarbinol, sulphuric acid reaction, 117.
Triphenylmethyl radical, 116.
Tritetracontane, 71.

United States:
  crude oils, 3–20.
  crude oil reserves, 43.
  drilling statistics, 43.
  crude oil production, 43, 44, 48.
  oil consumption, 48, 49.
  oil exports, 48, 49.
  oil prices, 51.
  refinery output, 48.
U.S.S.R.:
  crude oil production, 44.
  oil supply position, 50.

Venezuela, crude oil:
  analyses, 21.
  production, 43, 44.
Viscosity-gravity constant, 36.
Viscosity index, 36.

Wax, petroleum:
  content in crude oil, 69.
  cyclic hydrocarbons in, 72.
  isoparaffins in, 70.
  paraffins in, 69.
  types, 68.
Wax distillate, evaluation, 41.
World:
  crude oil:
    production, 43–6.
    reserves, 42.
  oil supply and demand, 47.
Wyoming, crude oil:
  analyses, 19.
  aviation base stock data, 11.
  production and reserves, 8.
  toluene and naphthene content, 13.

Xylene isomers, alkylation, 95.
Xylenes:
  aldehydes from, 92.
  free energy of formation, 156.
  oxidation, 94.
  sodium derivatives, 93.

PRINTED IN GREAT BRITAIN
AT THE UNIVERSITY PRESS, OXFORD
BY CHARLES BATEY, PRINTER TO THE UNIVERSITY